Chemical Stimulation of Oil Wells Producing from Carbonate Reservoirs

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Executive Summary

Oil reserves from shallow-shelf carbonate reservoirs account for 22% of the original oil in place of the entire U.S. oil resource, and many of these reservoirs are naturally fractured. About 40 years ago, a pressure-pulsing technique (spontaneous imbibition) with water was proven effective to recover oil from naturally fractured oil-wet fields. In some situations, imbibition of water can be promoted by chemical stimulation to alter the reservoir wettability toward water-wetness such that oil is expelled at an economic rate from the rock matrix into fractures. Many Class II shallow-shelf, carbonate reservoirs are naturally fractured, typically produce less than 10% original oil in place during primary recovery, respond poorly to water injection, and appear to be candidates for new surfactant-based technology.

The promotion of spontaneous imbibition was determined for a cationic and a nonionic surfactant. Cores from three dolomitic Class II reservoirs located in Wyoming, New Mexico, and Montana were used in the laboratory tests. After preparing over 150 core samples using the corresponding reservoir crude oil and brine, spontaneous expulsion of oil was measured in glass imbibition cells at reservoir temperature. When reservoir brine was used as the imbibition fluid, oil recovery was in the range of 0–35% of the original oil in place. After imbibition of reservoir brine had ceased, the cores were transferred into surfactant solutions at or above the critical micelle concentration to test for enhanced recovery by further imbibition. Typically, immersion in the surfactant solution resulted in additional recovery of 5–10% original oil in place. The increased recovery is mainly ascribed to increased water wetness. Laboratory experiments with cores and fluids from the Montana reservoir indicated that the reservoir was water-wet and, therefore, unsuitable as a candidate for the spontaneous imbibition process.

Following the laboratory imbibition cell experiments with the Wyoming field core, trials with producing oil wells were conducted to determine the effectiveness of nonionic surfactant soak treatments as a single-well, enhanced oil recovery technique. The trials were conducted in the dolomite interval of the Phosphoria formation. Artificial intelligence was applied to analyze the mixed test results. Fuzzy logic and neural networks were the artificial intelligence tools applied to the field dataset. For the first time, fuzzy ranking was used to evaluate the volume and amount of chemical used in each well. It was determined that a minimum cut-off amount of surfactant is required to improve production. The analysis suggested that the gamma ray and neutron logs can be used to predict treatment results. A method was developed to maximize the incremental oil resulting from a well treatment by adjusting the quantity of chemical applied. A single field test was conducted with a cationic surfactant. The field test sustains the laboratory observation that the nonionic surfactant performance is superior to the cationic. The value of neural network method to predict surfactant soak performance was confirmed with the cationic surfactant trial.

The economics of the field trails do not justify expansion to all wells; however, the neural network correlations suggested that the success rate could be improved to 80% at which point the technology is economic. An outside consulting company concluded that the technology could be commercialized. Discussions are progressing with two specialty oilfield service companies interested in utilizing the technology.

Introduction and Background

The primary technical objective of Phase II was to determine the feasibility of correlating field experimental variables including pseudo logs and the dynamic production data with incremental oil recovery resulting from large-scale tests in order to predict oil recovery.

The secondary objectives were as follows:

- To test the process under different reservoir systems.
- To investigate imbibition with surfactant mixtures.
- To study the effects of surfactant concentration on the imbibition process.
- To study the effect of temperature on the surfactant imbibition process.
- To develop a laboratory system utilizing sidewall cores (1” diameter).
- To simulate successive field soak treatments.
- To determine the effect of acid on surfactant enhanced imbibition oil recovery.

The first part of the final report (Chapters 1–3) for Phase II of the project “Chemical Stimulation of Oil Wells Producing from Carbonate Reservoirs” covers the laboratory work. The second part (Chapter 4) covers the field results. The following laboratory tests were performed during the past 2 years:

1. Laboratory imbibition tests with Yates Dagger Draw field reservoir fluids and cores: 11 cores plugs were tested with the crude oil, reservoir brine, and three types of surfactants.

2. Laboratory imbibition tests for Cottonwood Creek field reservoir fluids and cores: 39 core plugs from the Cottonwood Creek field were tested with the crude oil, modified reservoir brine, and five different surfactants along with mixtures of surfactants and acidized brine solutions.

3. Laboratory imbibition tests with Lustre field reservoir fluids and cores: 50 core plugs from Lustre field were tested with two different crude oils, one modified crude oil, and the reservoir brine solution; and 10 different surfactants and mixtures of surfactants.

4. Laboratory imbibition tests for an outcrop carbonate rock: 40 core plugs from an outcrop carbonate rock–West Texas Creme, were tested with two different crude oils and brine solutions, and 10 different surfactants.

Different procedures and chemicals were used for different rock/brine/oil systems, and the report first lists the surfactants used throughout the work. The properties of the rock, brine, and oil; experimental procedure; and test results for each rock system were introduced accordingly.

The focus of the second part of the report is the use of artificial intelligence (AI) to evaluate the results of the field experiments. Since the use of AI (comprised of fuzzy logic and neural networks) as an engineering technique is recent, an overview of the AI tools used to perform the analysis follows.

Fuzzy logic, used as a ranking tool for neural network inputs, is a powerful new analytical tool. Ali et al. (1997) applied fuzzy logic to a core dataset consisting of measured properties; Balch et al. (1999) later defined fuzzy logic as a ranking tool for neural network inputs.

To understand the principles for application of fuzzy logic, consider a dataset consisting of two variables x and y, where y is the random value of x or y_i = random (x_i) (by definition the dataset is 100% noise) (Fig. 0-0-1). For each data point (x_i, y_i), a "fuzzy membership function, $F_i(x)$" is defined using the following relationship:

$$F_i(x) = \exp(-(\frac{x_i - x}{b})^2) \bullet y_i$$

Wherein:

x = input variable
i = 1,2,3…N
N = Total number of input pairs
y_i = random (x_i) or desired output variable; and
b_i is a parameter that defines the influence radius of the fuzzy membership function at x_i.

A fuzzy membership function is generated for each of the 100 random data points (Fig. 0-0-1). The two bell shaped curves in the figure are generated with a fuzzy membership function.

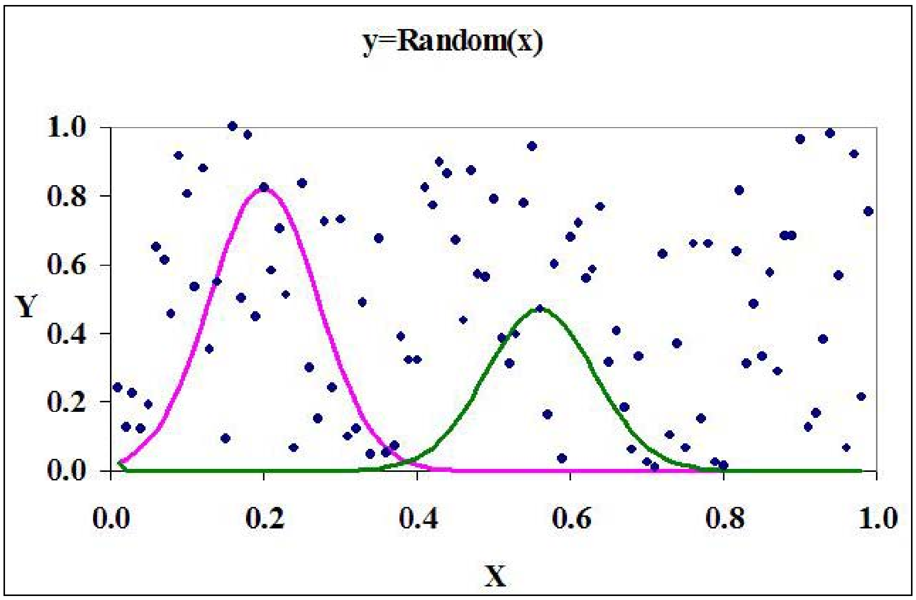


Fig. 0-0-1. Random dataset, 100 points. Fuzzy membership function is applied to two points.

The same fuzzy membership function is applied to a 100-point dataset with an $x^{0.5}$ trend added (Fig. 0-0-2).

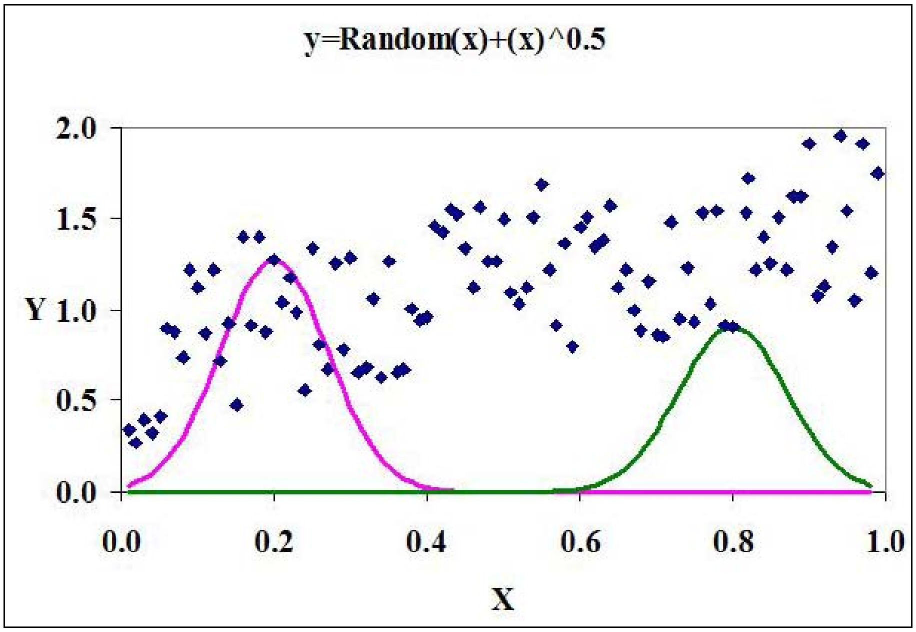


Fig. 0-0-2. Random dataset with x^2 trend added. Fuzzy membership function is applied to two points.

The fuzzy membership value is calculated for each output variable y using all available input data. These values are iteratively summed to obtain the fuzzified values of the input dataset with respect to each of the desired output y. These values are then defuzzified to generate the fuzzy curves (Fig. 0-0-3) by using the fuzzy curve function, *FC(x)*.

$$FC(x) = \frac{\sum_{i=1}^{N} F_i(x)}{\sum_{i=1}^{N} F_i(x) / y_i}$$

$F_i(x)$ is the fuzzy membership function for each input x;

Wherein:

i = 1,2, . . .N

N = Total number of input pairs

y_i = F(random (x_i)).

The final curve can be interpreted by using given inputs for linear or nonlinear regressions as well as by providing additional insight to potential relationships.

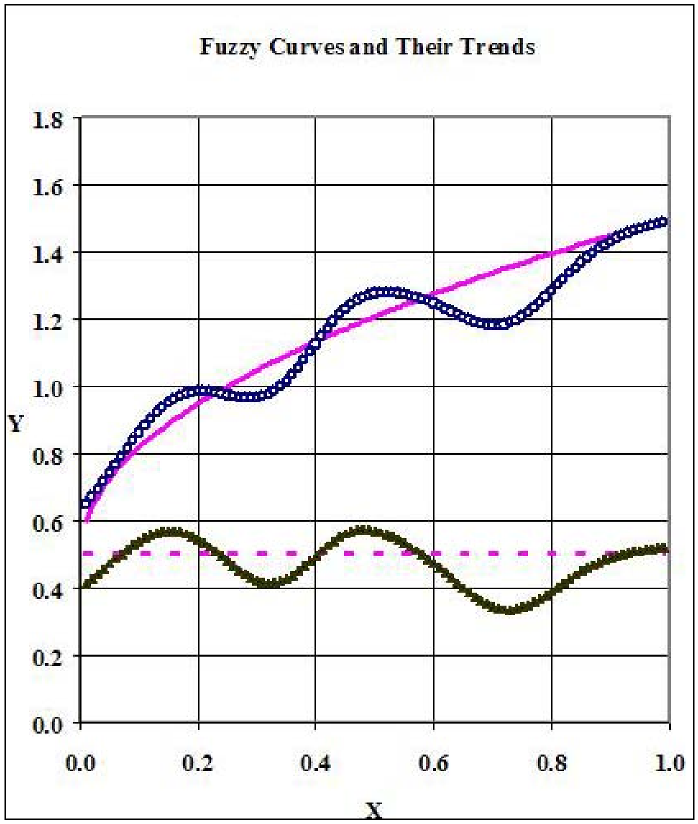


Fig. 0-0-3. Variables with a trend, top curve, are readily identified with fuzzy curves.

The fuzzy curve generated with the 100% noisy (random) dataset (Fig. 0-0-3, lower curve) exhibits no correlation between x and y and, therefore, would not be considered as a reliable neural network input variable. The fuzzy curve generated with the noisy dataset that included a square root of x trend (Fig. 0-0-3, upper curve) shows that as x increases, so does the fuzzified y value. Hence, fuzzy logic can differentiate between datasets that exhibit a relationship between variables from those that do not. The difference between the maximum and minimum values of the fuzzified variable y, also called the "range," indicates the strength of the relationship between the two variables. The "goodness" of the fuzzy curve can be estimated by adding the value of the "least square fit" correlation coefficient to the value of the fuzzy curve range. For example, in Fig. 0-0-3, the range of the fuzzy curve with the added trend is 0.9, the correlation coefficient of the best-fit line to the fuzzy curve data points is about 0.9, and the "goodness" is 1.8. Conversely, the fuzzy curve generated with random data has a range of about 0.2 and a least square fit line correlation coefficient of about 0.9, and the goodness is 1.1, much less than the trend data. Variables once selected from a dataset can be used as neural network inputs.

Neural networks (http://www-ra.informatik.uni-tuebingen.de/SNNS) are particularly well-suited for correlating multiple variables with experimental results. This makes them especially useful for the multiple variables that may be associated with field experiments. The Feed Forward Error Back Propagation neural network, because of its versatility, is widely applied to oilfield problems. It is accepted as the most generic and robust technique. Other techniques include Radial Basis Function and Kohonen neural networks. The networks consist of layers made of nodes. Input nodes include the variables thought to influence the output node variable. The nodes in each layer are linked by tie lines (weights) through transfer functions to all of its neighbors. The 2-2-1 architecture neural network (Fig. 0-0-4) has an input layer 1 with two nodes in1, in2; the hidden layer 2 has two nodes; and the output layer 3 has one node, Out1.

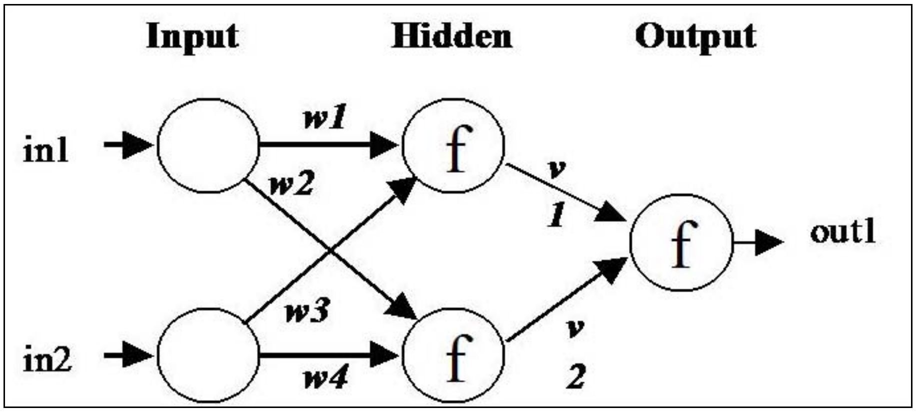


Fig. 0-0-4. 2-2-1 Neural network.

The weight of the tie lines connecting the nodes is denoted with w or v. The f node is the sigma function. This simple 2-2-1 neural network is represented by the following regression equation (Subramaniam, 2002):

$$Out1 = f(v1*f(w1*in1+w3*in2)+v2*f(w2*in1+w4*in2))$$

Wherein:

in1, in2 are input variables;
wn and vn are the values of the connecting weights of each layer; and
Out1 is the output/result.

Adjusting the strength of the weights to cause the overall network to output appropriate results accomplishes “learning” or “training” of the system. In the equation, the “inputs” to the network are typically represented by the mathematical symbol, in(n). Each input is multiplied by a “connection weight” at the hidden layer nodes and the output node, Out1. These weights are represented by w(n)… v(n) to connect the input in the hidden layer(s) to the output. In neural networks, the designer typically utilizes trial and error in the design decisions. A generalized matrix solution (Subramaniam, 2002) for one iteration through a neural network between any two layers in the network is given by the following equation:

$$Out1=Act*[W*In],$$

Wherein:

$$W = \left[\begin{array}{cc|c} W_{11} & W_{12} & W_{1i} \\ W_{21} & W_{22} & W_{2i} \\ \hline W_{k1} & W_{k2} & W_{ki} \end{array}\right]$$ is the weight matrix;

$$In = \begin{bmatrix} In_1 \\ In_2 \\ --- \\ In_i \end{bmatrix}$$ is the matrix of the input variables;

$$Out1 = \begin{bmatrix} Out1_1 \\ Out1_2 \\ ----- \\ Out1_k \end{bmatrix}$$ is the output matrix at each layer; and

$$Act = \left[\begin{array}{cc:c} f_{11} & 0 & 0 \\ 0 & f_{22} & 0 \\ \hdashline 0 & 0 & f_{ki} \end{array}\right]$$ is a nonlinear diagonal activation function matrix;

i = Total number of inputs to a given layer;
k = Total number of nodes in a given hidden/output layer;
W_{ki} = Weight that connects the output of the i'th input node to the Input of the k'th hidden node.

Applying this matrix multiplication to a simple 2-2-1 neural network (Fig. 0-0-4) results in the following regression equation as shown earlier.

$$Out1 = f(v1*f(w1*in1+w3*in2)+v2*f(w2*in1+w4*in2)).$$

Determining the number of hidden neurons best used in the network is an important procedure in neural network design. If the hidden number of neurons is increased too much, overtraining will result in the network being unable to "generalize." The training dataset will be memorized, making the network effectively useless on new datasets. The overtraining problem is illustrated with the example in Fig. 0-0-5 from Weiss et al. (1999). Notice that none of the polynomial training values is negative, yet the training curve could generate a negative answer.

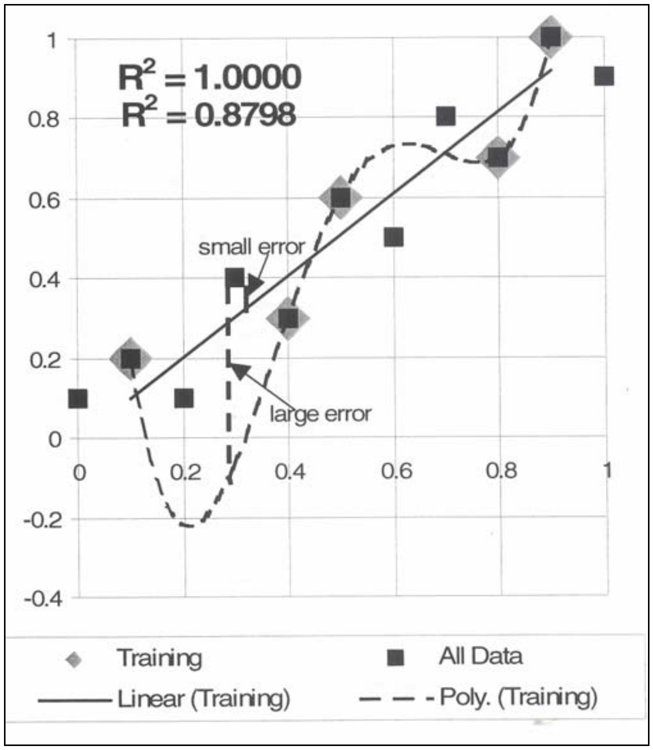


Fig. 0-0-5. Overtraining example. None of the polynomial training values is negative, yet the perfect training curve could generate a negative value (Weiss et al., 1999).

Du et al. (2003) investigated the overtraining problem with a series of synthetic datasets similar to those shown in Figs. 0-0-2 and 0-0-3. The work of Du and colleagues (2003) was based on well-controlled synthetic datasets with noise added. They evaluated six different functions as synthetic datasets of x to describe y. One example used a value of x as the input, and the output, y, was ((x^2+1) + random x). It was found that a 1-3-4-1 neural network (19 weights) trained to about 100% using 12–480 values of y (training records). Ten percent of the values of y (outputs) were parsed for testing purposes. Du et al. (2003) found that the trained 1-3-4-1 neural network predicted correct values for the parsed values about 100% of the time until the number of training records fell below 32 (a 1.7 weights-to-records ratio). When the number of training records was decreased to 24, the testing correlation coefficient fell to 72%. This exercise was repeated with six different functions including sin(x), sin(x)*cos(x)/2, and three Fourier functions serving as values of y (outputs). In all cases, exceeding the weights-to-records ratio of 2.0 resulted in poor testing performance or overtraining.

A neural network can be designed in a constructive or destructive manner. The constructive technique begins with the input values initially connected to the output by a single layer with one node. The training run is conducted, and if the training is poor, another node or layer is added (maintaining a weights-to-records ratio less than two) until training is satisfactory. The destructive technique begins with a complex architecture (with a weights-to-records ratio less than two), and the complexity is reduced after each training run.

Chapter 1. Surfactants

In the laboratory work, cationic, nonionic, and anionic surfactants were added to the synthetic reservoir brine to improve spontaneous imbibition oil recovery. The chemical names, formula, and critical micelle concentration (CMC), etc. of the surfactants are listed in Tables 1-1-1, 1-1-2, and 1-1-3. The interfacial tensions (IFTs) between oil and brine were measured by the du Nouy ring method (IFT > 1 dynes/cm), the drop volume method (0.1 < IFT < 1), or the spinning drop method (IFT < 0.1) according to the range of the IFTs.

Table 1-1-1. Physical and chemical properties of cationic and nonionic surfactants

Properties	**Arquad 12-50***	**Arquad C-50***	**Tomadol 91-8****	**Triton X100****
Chemical name	Dodecyltrimethyl ammonium chloride or (N,N,N-Trimethyl-1-dodecaminium chloride)	Cocoalkyltri me-thyl ammonium chloride	Poly (2.5 or 6 or 8) oxyethylene C_{9-11} alcohol	Octylphenol ethylene oxide condensate
Designated in this report	A12-50	C-50	T91-8	X100
Chemical formula	$C_{12}H_{25}N(CH_3)_3Cl$ or $RN(CH_3)_3Cl$	$R_2N(CH_3)_3Cl$ R = cocoalkyl	$ROCH_2CH_2O)_nH$ $R = C_9/C_{10}/C_{11}$	$C_{14}H_{19}O(C_2H_4O))_nH$ ($n \approx 9.5$)
Chain length	12	12–16	9–11	~9.5
Equivalent weight	263	278	524	625
pH	6–7	6–7	-	6–8 (5% solution)
Flash point, °C	19	19	159	-
Surface tension at 0.1 mol, dynes/cm	33	31	30	-
Initial boiling point, °C	80 at 760 mmHg	80 at 760 mmHg	-	-
Melting point, °C	-10	-9	7–24	-
CMC at 30 °C	20 m mol or 5260 ppm	Less than 1 m mol or 278 ppm	About 1 m mol at 25°C, or 524 ppm	0.220.24 m mol or 138–150 ppm
Commercial concentration, (wt%)*	~ 45–55	~ 45–55	~ 100	~ 97

*Commercially supplied Arquad 12-50 and Arquad C-50 contain about 30–35% of CH_3-CH_3-CHOH and 10–20% of water besides the surfactants.

**The hydrophilic and lipophilic balance value: $HLB_{T91-8} = 13.9$, $HLB_{X100} = 13.5$.

Table 1-1-2. Physical and chemical properties of anionic surfactants			
Properties	**5-67PS**	**5-69PS**	**5-70PS**
Chemical name	Alcohol ether sulfonate	Alkylphenol ether sulfonate	Alkylamine ether sulfonate
Chemical formula	R^1 [-(O-(R^2O)m-(R^3O)n-(R^4)]$_y$ R^1 = alcohol R^2 , R^3, R4 *	R^1 [-(O-(R^2O)m-(R^3O)n-(R^4)]$_y$ R^1 = alkylphenol R^2 , R^3, R4 *	R^1 [-(O-(R^2O)m-(R^3O)n-(R^4)]$_y$ R^1 = alkylamine R^2 , R^3, R4 *
CMC at 30 °C	0.1%	0.1%	0.1%
Supplied concentration, wt%	50% active	25% active	30% active

*R^2 , R^3 = C_2H_4 or C_3H_6 or C_4H_8
R^4 = linear or branched $C_7H_{14}SO_3X$ to $C_{30}H_{60}$ SO_3X when y = 1,
R^4 = linear or branched $C_7H_{14}SO_3$ X to $C_{30}H_{60}$ SO_3X or H when y > 1, but at least one R^4must be linear or branched $C_7H_{14}SO_3X$ to $C_{30}H_{60}$ SO_3X,
m ≥ 1, n ≥ 0, n + m = 1 to 30+, y ≥ 1.

Table 1-1-3. Other surfactant properties			
Commercial name	**Chemical name**	**Ionic type**	**CMC, wt%**
IMB-110	-	Anionic	0.01
5-163	-	Anionic	
AES 506	-	Anionic	0.01
AES 205	-	Anionic	0.01
S-31-T	Amino methylene phosphonate	Scale inhibitor (water soluble)	-
SC-900	Polymer	Dionic, shale stabilizer (partial soluble in water)	-
NCL-100	Quaternary chloride	Cationic, clay inhibitor (completely water soluble)	-
Witconate 3203	-	Anionic	~ 1.1
Witcolate 1276	Fatty amine derivative	Anionic	~ 0.25
2C-75		Cationic	

Chapter 2. Experimental Tests and Results

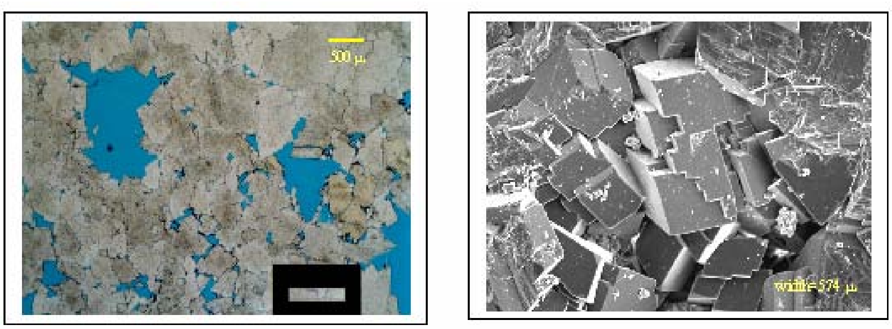
Section 1. Yates Dagger Draw Oilfield

Cores: Eleven core plugs 1.5” (~3.8 cm) in diameter were cut from Dagger Draw core material from the upper Pennsylvanian dolomite zone. The reservoir temperature was 130 °F. The air permeabilities ranged from less than 0.1 to about 25 md, and porosities ranged from about 6–11% (Table 2-1-1). These values are consistent with the porosity and permeability data provided by the Yates Petroleum Corporation. Thin section and scanning electron microscope (SEM) pictures (Fig. 2-1-1) indicate that the pores in Dagger Draw rock are intercrystal spaces that resulted from dolomitization of carbonate rocks.

Table 2-1-1. Properties of Yates Dagger Draw cores

Core No.	Depth, ft	L, cm	K_g, md	ϕ, %	S_{wi}, %	Surf. used and concentration, ppm	AR = ϕ/k_g, md^{-1}	BVO = $\phi(100 - S_{wi})$
Y1	7714	6.65	1.34	6.9	24.1	C-50, 500	5.15	5.24
Y2	7682.9	6.15	1	8.9	6.4	T91-8, 750	8.9	8.33
Y3	7682.8	6.95	2.7	7.5	6.3	A12-15, 7500	2.78	7.03
Y4	7682.7	6.02	3.9	10.2	55.8	T91-8, 750	2.62	4.51
Y5	7717.6	6.49	24.7	10.8	41.8	A12-15, 7500	0.44	6.29
Y6	7717.8	4.77	8.4	10.3	35.8	C-50, 500	1.23	6.61
Y7	7717.9	6.55	0.29	9.23	0	T91-8, 750	31.83	9.23
Y8	7574.7	5.26	0.4	7.1	0	A12-50, 7500	17.75	7.1
Y9	7574.8	5.83	0.2	5.6	0	A12-50, 7500	28	5.6
Y10	7574.9	5.7	0.45	5.63	0	C-50, 500	12.51	5.63
Y11	7683.8	5.52	0.02	3.42	0	C-50, 500	171	3.42

AR = aspect ratio
BVO = bulk volume oil



(a) Thin section (b) SEM (574 μ)

Fig. 2-1-1. Thin section and SEM pictures for Dagger Draw rock.

Oil: The Dagger Draw oil is semi-opaque and yellow-to-brown in color. The oil was purged with nitrogen to remove H_2S prior to laboratory studies. The density was 0.8024 g/ml (44.8 °API) at ambient temperature and 0.766 g/ml at a reservoir temperature of 130 °F (55 °C). The viscosity was 2.4 cp at ambient temperature and 1.4 cp at reservoir temperature. The heptane-asphaltene content of the oil was undetectable.

Brine: Yates Petroleum Company provided the analysis of Dagger Draw reservoir water. However, in attempts to reconstitute brine with this composition, dissolution of the component salts was incomplete. Yates Petroleum Company provided another sample of brine, and it was analyzed at the University of Wyoming (UW). The analysis obtained from UW differed in many respects from the provided analysis (Table 2-1-2). Reformulated brine used in the experiments was based on the UW analysis and is designated as Yates brine. IFTs are listed in Table 2-1-3.

Table 2-1-2. Brine composition of Dagger Draw field		
Components	**Yates analysis, g/L**	**UW analysis, g/L**
$Ca(HCO_3)_2$	1.053	-
$MgCl_2$	2.381	0.3327
$CaCl_2$	0.290	1.0124
$CaSO_4$	2.835	-
NaCl	5.549	2.072
$NaHCO_3$	-	0.011
Na_2SO_4	-	2.7682
KCl	-	1.0628
Density@ 21°C	~ 1.0	1.0054
TDS, g/L	12.108	6.1963

Table 2-1-3. Concentrations and interfacial tensions of the Yates brine and oil			
Brine	**Concentration, ppm**	**Equivalent concentration of commercially supplied, lb/bbl**	**IFT at ambient temp. dynes/cm**
Yates brine	-	-	8.4
Arquad 12-50 solution *(Arquad 12-50 in Yates brine)*	7500	5.26	0.6
Arquad C-50 solution *(Arquad C-50 in Yates brine)*	500	0.36	0.3
Tomadol 91-8 solution *(Tomadol 91-8 in Yates brine)*	750	0.27	2.0

Experimental procedure:

a) Air permeability measurement: Air permeability was measured with nitrogen gas for each clean core using Hassler core holders.

b) Porosity measurement: All the cores were saturated with test brine by vacuum. Porosity was measured from the increase in weight. The cores were immersed in brine for 7–10 days to allow ionic equilibration.

c) Establishment of initial water saturation: The initial water saturation, S_{wi}, was about 10–15% from well log analysis. S_{wi} for some of the cores was established by displacement of crude oil, and for others by drainage using the porous plate method. The porous plate pressure was set between 15–160 psi. After drainage of the brine by air, the core was evacuated and then saturated with crude oil. Some cores were directly saturated with the crude oil.

d) Aging: The cores were then immersed in crude oil in aging cells. A gravimetric check was used to confirm that the cores were fully saturated with liquid. For any core plug not fully saturated with brine and crude oil, a pressure of about 1000 psi was applied to the aging cell to ensure full saturation. Then the aging cells were set in an oven. All of the cores were aged for 10 days at reservoir temperature, 130 °F (~ 55 °C).

e) Imbibition test: After aging, each aged core was submerged in lab brine in an imbibition cell (see Fig. 2-1-2). All imbibition tests were performed at reservoir temperature (130 °F for Yates cores and 140 °F for Cottonwood Creek cores). Oil recovery by imbibition versus time was recorded. Most cores stopped producing oil by imbibition of synthetic brine within 7 days, or about 7–10 days. The cores were then immersed in surfactant solutions, and measurements of oil recovery versus time were continued.

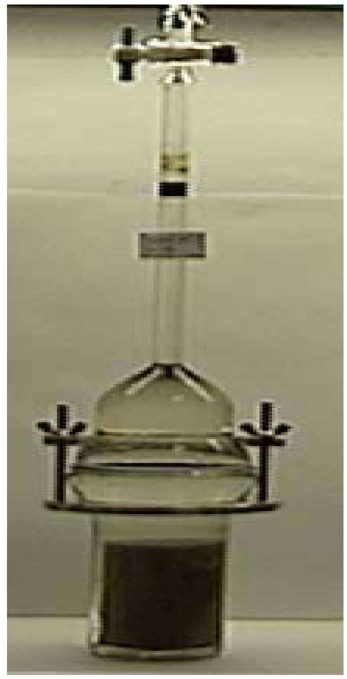


Fig. 2-1-2. Imbibition cell.

Test results: After each core was immersed in the lab brine for 10–15 days, less than 10% of the original oil in place (OOIP) was produced (only 1.5% OOIP was produced from core Y2), except for core Y4 for which imbibition oil recovery was about 15% OOIP. Core Y4 had the highest initial water saturation (55.8%) in the group. In most cases, imbibition of Yates brine ceased after 5 days. The brine was then replaced by surfactant solution (see Table 2-1-1 for the surfactants and concentrations). Plots of imbibition time versus oil recovery are shown in Figs. 2-1-3, 2-1-4, and 2-1-5. After the surfactant solution was introduced, oil production by imbibition was at least doubled in most cases. The cores with an initial water saturation showed better response to surfactant than those without. Overall, the nonionic surfactant T91-8 was more effective than the other two surfactants (Figs. 2-1-6 and 2-1-7), and this is consistent with Phase I results. Generally cores with higher porosity, permeability, and initial water saturation gave higher oil recovery. The relationships between final oil recovery versus bulk volume of oil and aspect ratio are scattered, but the trend can still be seen: the higher the oil recovery, the higher the bulk volume of oil, and the lower the aspect ratio (Fig. 2-1-8). It is worth pointing out that the IFT of the Dagger Draw crude oil/brine was only 8.4 dynes/cm, and it is likely that the crude oil was contaminated. It is, therefore, possible that the contaminant affected the imbibition of brine.

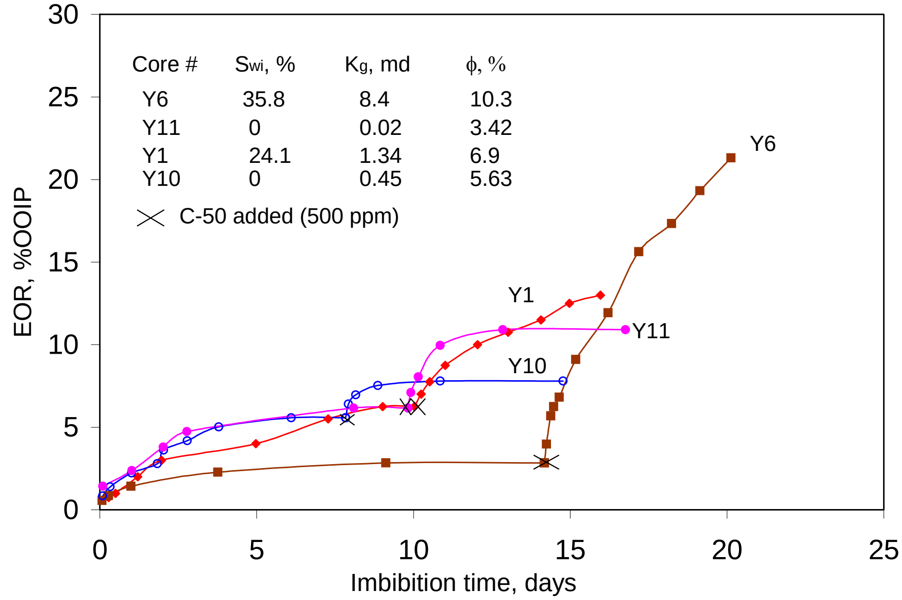


Fig. 2-1-3. Response of oil recovery by spontaneous imbibition to cationic surfactant C-50.

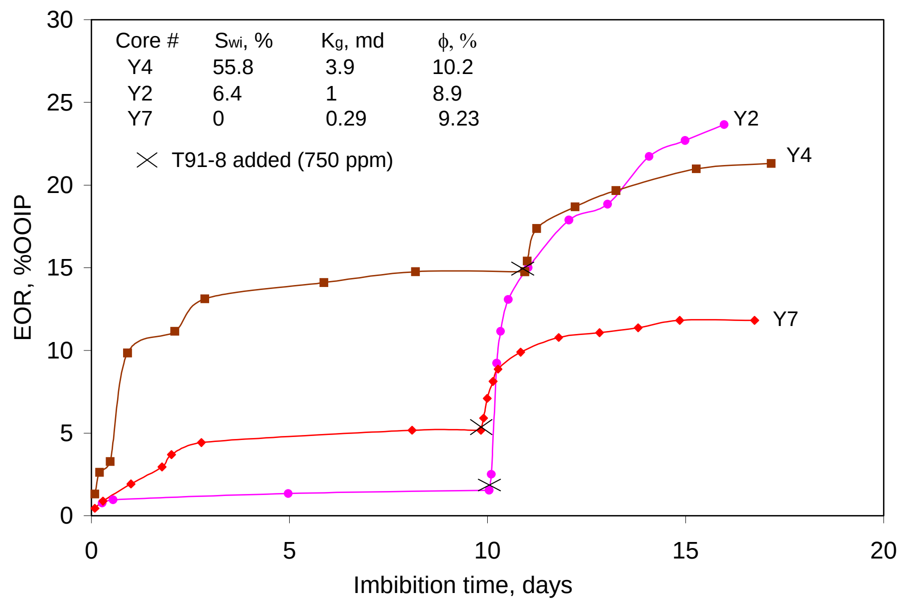


Fig. 2-1-4. Response of oil recovery by spontaneous imbibition to nonionic surfactant T91-8.

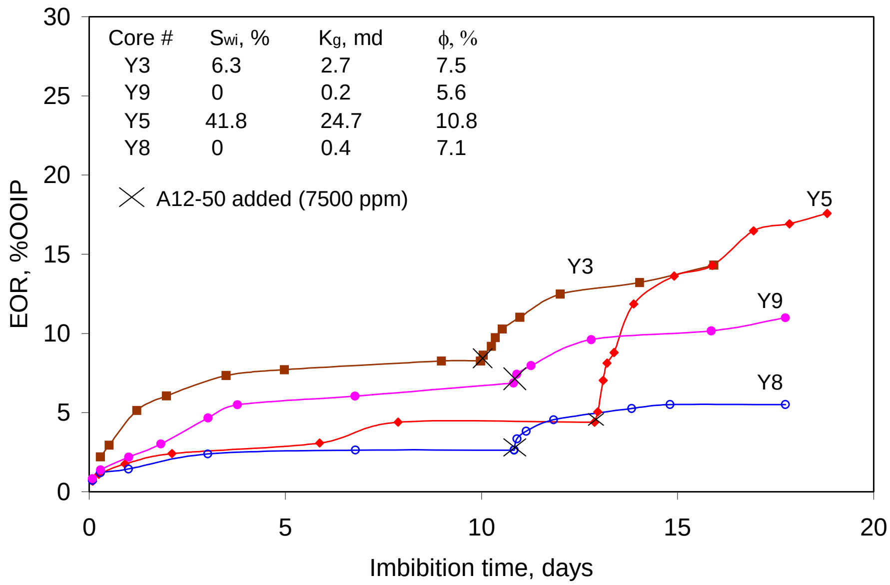


Fig. 2-1-5. Response of oil recovery by spontaneous imbibition to cationic surfactant A12-50.

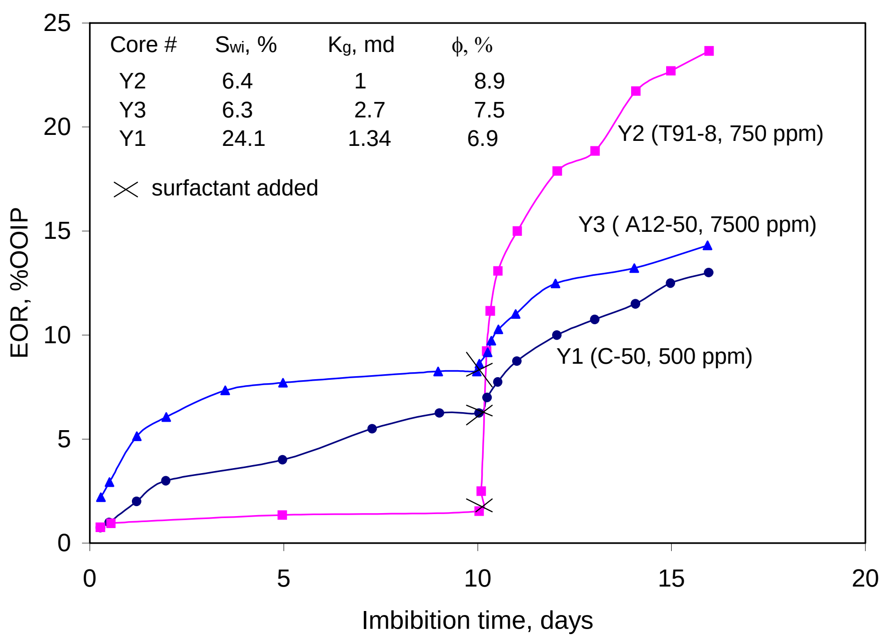


Fig. 2-1-6. Comparison of oil recovery by imbibition for two cationic and one nonionic surfactant solutions for cores containing initial water.

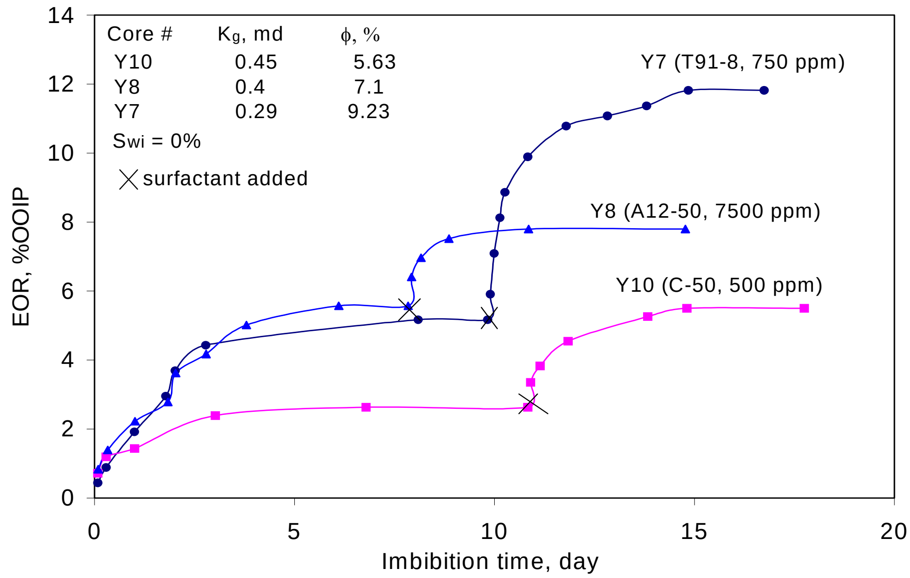


Fig. 2-1-7. Comparison of oil recovery by imbibition for two cationic and one nonionic surfactant solutions for cores without initial water.

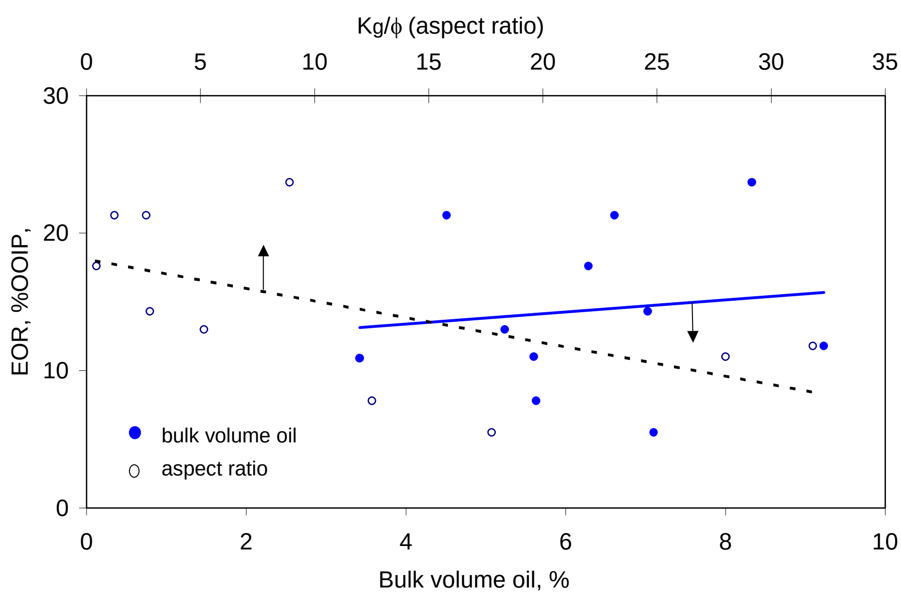


Fig. 2-1-8. Surfactant oil recovery as a function of aspect ratio and bulk volume oil for Yates cores.

Section 2. Cottonwood Creek Oilfield

The objective of the experiments was to test the effect of concentration of cationic surfactant C-50 on imbibition recovery and the presence of HCl on surfactant imbibition oil recovery.

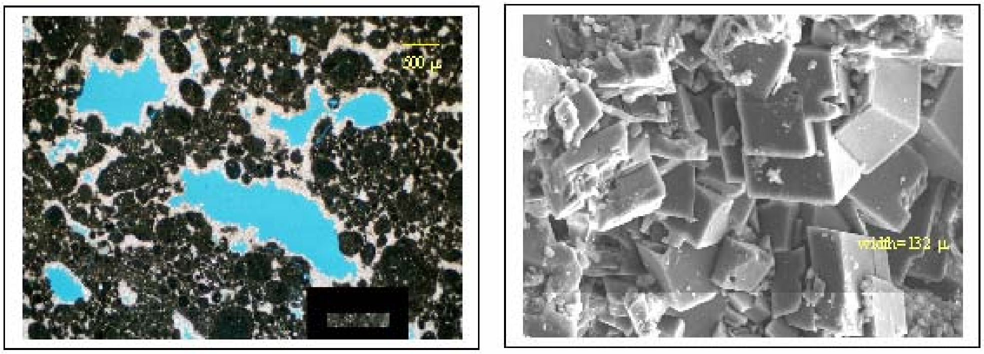
Cores: Core plugs were from two sources. One batch of plugs with 1" (~ 2.54 cm) diameter was provided by the operating company, Continental Resources, Inc. Another batch with 1.5” (~ 3.8 cm) diameter was cut from the Cottonwood Creek field CCU #210 whole core material. The air permeabilities ranged from 0.2 to about 130 md and porosities from about 3% to 21% (Tables 2-2-1 and 2-2-2). Most of the cores appeared to be very heterogeneous, some cores had fractures and vugular pores. The presence of fractures was also suspected for cores that exhibited unusually high permeabilities. Petrographic thin sections and SEM pictures (Fig.2-2-1) indicate that the pores in the Cottonwood Creek rock vary in size and are lined by sparry dolomite crystals. These pores consist of the spaces that remain after cementation of carbonate grains.

Table 2-2-1. Properties of cores with a 1" diameter

Core No.	L, cm	K_g, md	ϕ, %	S_{wi}, %	C_{C-50}, ppm	Acid added, wt%	AR = ϕ/k_g, md^{-1}	BVO = $\phi(100-S_{wi})$
255-21	5.05	52.7	17.6	0	500	2	0.33	17.6
255-25	5.01	9.8	16.1	0	500	1.0	1.64	16.1
255-14	5.03	3.6	17.4	0	500	0	4.83	17.4
255-42	4.62	5.7	12.5	0	500	2	2.19	12.5
255-4	4.92	88.4	8.7	0	500	1.0	0.1	8.7
255-27	5.06	13.1	9.5	0	278	0	0.73	9.5
255-30	3.89	21	12.8	0	700	0	0.61	12.8
255-26	5.04	3.41	12.8	0	278	0	3.75	12.8
255-5	4.21	5.5	10	0	500	0.5	1.82	10
255-18	4	11.1	13	0	150	0	1.17	13
255-9	5.02	9.1	13.3	0	75	0	1.46	13.3
255-3	5.09	12.8	14.7	14.1	150	2	1.15	12.63
255-15	5.0	12.3	13.7	23.5	278	0	1.11	10.48
255-24	4.89	2.2	13.9	26.2	500	0.5	6.32	10.26
255-12	4.962	3.8	13.9	22.1	700	1	3.66	10.83
255-23	4.26	22.9	16	7.6	278	0	0.7	14.78

Table 2-2-2. Properties of cores with a 1.5" diameter

Core No.	Depth, ft	L, cm	K_g, md	ϕ, %	S_{wi}, %	C_{C-50}, ppm	Acid added, wt%	AR = ϕ/k_g, md^{-1}	BVO = $\phi(100-S_{wi})$
2-1AC	5843.7	5.57	5.6	9.8	0	75	0	1.75	9.8
2-2AC	5843.8	5.12	6.4	10.6	0	150	0	1.66	10.6
2-3AC	5846.9	4.01	1.5	15.8	0	278	0	10.53	15.8
2-4AC	5843.1	5.6	2.4	9.8	0	500	0.5	4.08	9.8
2-5AC	5845	5.86	0.2	7.8	0	700	0	39	7.8
2-6AC	5848.6	5.12	129.4	13.7	9.6	75	0	0.11	12.38
2-7AC	5839.9	5.97	18.9	13	15.3	150	0	0.69	11.01
2-8AC	5834.5	5.41	74.2	12.1	25.9	278	0	0.16	8.97
2-9AC	5835.5	5.71	16.8	11.4	17.8	150	0	0.68	9.37
2-10AC	5844	5.85	31.3	11.54	14.4	700	0	0.37	9.88
2-11AC	5843	3.99	77.9	6.4	26.3	700	0	0.08	4.72



(a) Thin section (b) SEM (132 μ)

Fig. 2-2-1. Thin section and SEM pictures for Cottonwood Creek rock.

<u>Oil</u>: Cottonwood Creek crude had a gravity of 30° API. It contained 31.2% paraffins, 25.7% naphthenes, 43.1% aromatics, and 2.3% heptane asphaltenes. The oil samples used in laboratory testing were collected at the wellhead and purged with nitrogen to remove most of the H_2S. The acid number of the oil was 0.56 mg KOH/g oil, and the base number was 1.83 mg KOH/g oil. The density was 0.890 g/ml at ambient temperature. The oil viscosity was 24.3 cp at ambient temperature and 12.3 cp at reservoir temperature (60 °C).

<u>Brine</u>: The Cottonwood reservoir brine is composed of fresh water and dissolved carbonate or anhydrite from the Phosphoria formation. The total dissolved solids in the brine were about 24,000 ppm. Two analyses for produced brine from Cottonwood Creek are listed in Table 2-2-3. In reformulating these brines, it was found that not all of the salts dissolved. After discussion of this solubility problem with all parties, modified brine was prepared and is indicated as Lab brine in Table 2-2-3. Basically the carbonate and bicarbonate salts were excluded to avoid precipitation of $MgCO_3$ and $CaCO_3$. The sulfate content was also reduced to 25% of the original quantity in the Cottonwood-2 brine analysis. The density of the lab brine was 1.0189 g/ml.

Table 2-2-3. Brine composition for Cottonwood reservoir

Components	Cottonwood-1, g/L	Cottonwood-2, g/L	Lab brine, g/L
$CaCl_2$	6.0917	8.402	8.4043
$MgCl_2$	1.5835	1.586	1.5868
Na_2SO_4	3.8903	6.786	1.7647
KCl	0.3623	0	0
NaCl	8.7239	7.443	19
Na_2CO_3	0	0.4155	0
$NaHCO_3$	3.025	4.1554	0
TDS, g/L	23.677	28.7879	30.7558

<u>Procedure:</u>

a) Air permeability measurement: Air permeability was measured with nitrogen gas for each clean core using Hassler core holders.

b) Porosity measurement: All the cores were saturated with test brine by vacuum. Porosity was measured from the increase in weight. The cores were immersed in brine for 7–10 days to allow ionic equilibration.

c) Establishment of initial water saturation: The initial water saturation, S_{wi}, was about 10–15% from well log analysis. S_{wi} for some of the cores was established by displacement of crude oil, and for others by drainage using the porous plate method. The porous plate pressure was set between 15–60 psi. After drainage of brine by air, the core was evacuated and then saturated with crude oil. Some cores were directly saturated 100% with the crude oil.

d) Aging: The cores were then immersed in crude oil in aging cells. A gravimetric check was used to confirm that the cores were fully saturated with liquid. For any core plug not fully saturated with brine and crude oil, a pressure of about 1000 psi was applied to the aging cell to ensure full saturation. Then the aging cells were set in an oven. All of the cores were aged for 10 days at reservoir temperature, 140 °F (60 °C).

e) Imbibition test: After aging, each aged core was submerged in lab brine in an imbibition cell. All imbibition tests were performed at reservoir temperature. Oil recovery by imbibition versus time was recorded. Most cores stopped producing oil by imbibition of synthetic brine within 7 days, or about 7–10 days. Most cores were then immersed in surfactant solutions, and measurements of oil recovery versus time were continued.

f) Introduction of acid solutions in surfactant solutions: Initially, 15% HCl was used to clean the iron sulfide from the annular surface of the Cottonwood Creek field production wells prior to the addition of surfactant solution. To mimic the field situation, HCl was used in the laboratory imbibition tests. In the lab, three 1.5" in diameter cores from the Cottonwood field were used for strong acid solution soaking tests. The cores were saturated with the Cottonwood reservoir brine and crude oil (Table 2-2-4). After aging for 10 days at 60 °C, the cores were immersed in 15% HCl solution at the reservoir temperature. As soon as the cores contacted the acid solution, the acid and the carbonate core quickly generated heat. Crude oil was produced along with dissolved core material, and a scum was formed at the surface of the acid solution. The cores disintegrated into clean fragments in only a few minutes (surfaces were free of crude oil). The cores were then immersed in C-50 and T91-8 surfactant solutions at 60 °C for imbibition. No imbibition recovery was observed. This test indicated that the acid treatment is not appropriate for the small-scale lab tests.

Table 2-2-4. Properties of cores from the Cottonwood field

Depth, ft	Length, cm	K_g, md	ϕ, %	S_{wi}, %	Surfactant used
5841.2	5.02	22.6	8	0	T91-8
#1	4.41	28.6	11.6	22.85	C-50
5850.3	3.73	266.9	14.3	21.34	T91-8

Much weaker HCl solutions, with concentrations of 0.5, 1, and 2 wt%, were employed in the lab imbibition tests for Cottonwood Creek cores. The addition of HCl in the surfactant solutions did not change the IFT (Table 2-2-5). The procedure was as follows: Six cores were first immersed in the lab brine for about 10 days and then transferred to C-50 brine with continued measurement of oil recovery by imbibition. These three cores were then transferred to HCl brine for further imbibition. The other three cores were transferred to HCl brine directly, and C-50 was added a few hours later (Table 2-2-6). The time after which the imbibition liquid was changed is indicated in Table 2-2-6 for all nine cores.

Table 2-2-5. Interfacial tensions of the lab brine and Cottonwood crude oil

Brine	**Concentration, ppm**	**Equivalent concentration of commercially supplied, lb/bbl**	**IFT at ambient temp., dynes/cm**
Arquad C-50 solution *(C-50 in lab brine)*	0	0	31.96
	75	0.06	9.9
	150	0.11	4.1
	278	0.2	1.4
	500	0.36	0.16
	700	0.49	0.13
	2620	1.834	0.13

Table 2-2-6. Cottonwood Creek cores with introduction of HCl during imbibition

Core #	**C_{HCl}, wt%**	**Time switched to HCl solution, day**	**$C_{C\text{-}50}$, ppm**	**Time switched to C-50 solution, day**
255-21	2	53	500	12.5
255-25	1	49.2		12.3
2-4AC	0.5	27.3		13.8
255-42	2	15.2		15.3
255-4	1	12.4		12.5
255-24	0.5	37.4		9.5
255-5	0.5	15.25		15.33
255-3	2	37.3	150	9.5
255-12	1	39.3	700	11.5

<u>Test results:</u>

a) C-50 concentration tests: A series of different concentrations, 75, 150, 278, 500, 700, and 2620 ppm of C-50, was used in testing cores that were initially saturated with crude oil (CMC of C-50 is 278 ppm). Except for the highest value, the same surfactant concentrations were also tested for cores containing 9.5%–17.4% initial water saturation (see Figs. 2-2-2 and 2-2-3). The highest recovery was obtained for core 2-6AC using the lowest concentration of surfactant. However, this particular core had much higher permeability than average. Overall, oil recovery increased with the concentration of C-50, but the results were very scattered (Fig. 2-2-4). Cores containing initial water saturation tended to be less sensitive to surfactant than those initially saturated with oil. Variation in core properties and the heterogeneity of individual cores, including the presence of fractures, probably contributed to the scatter in the results.

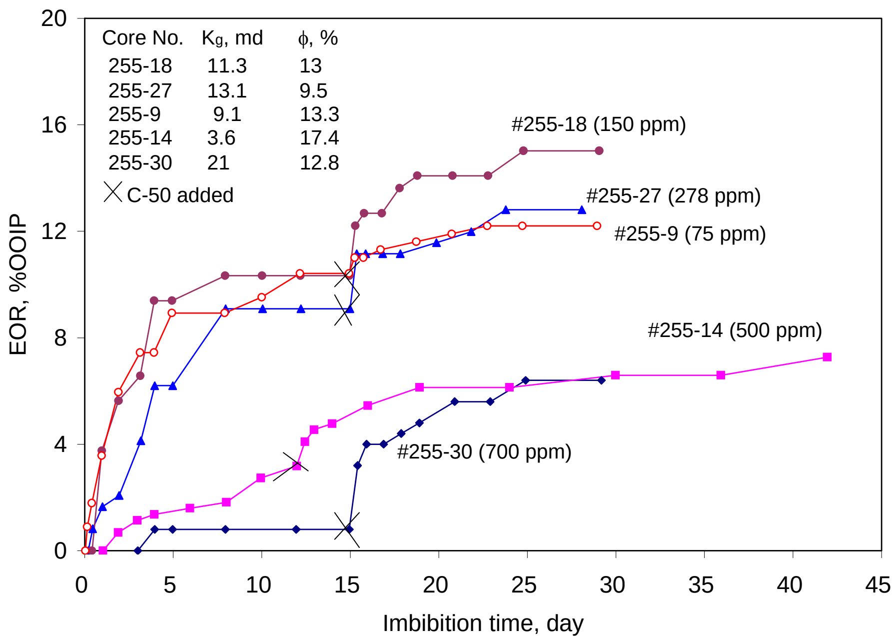


Fig. 2-2-2. The effect of C-50 concentration on Cottonwood oil recovery by imbibition from cores initially saturated with crude oil.

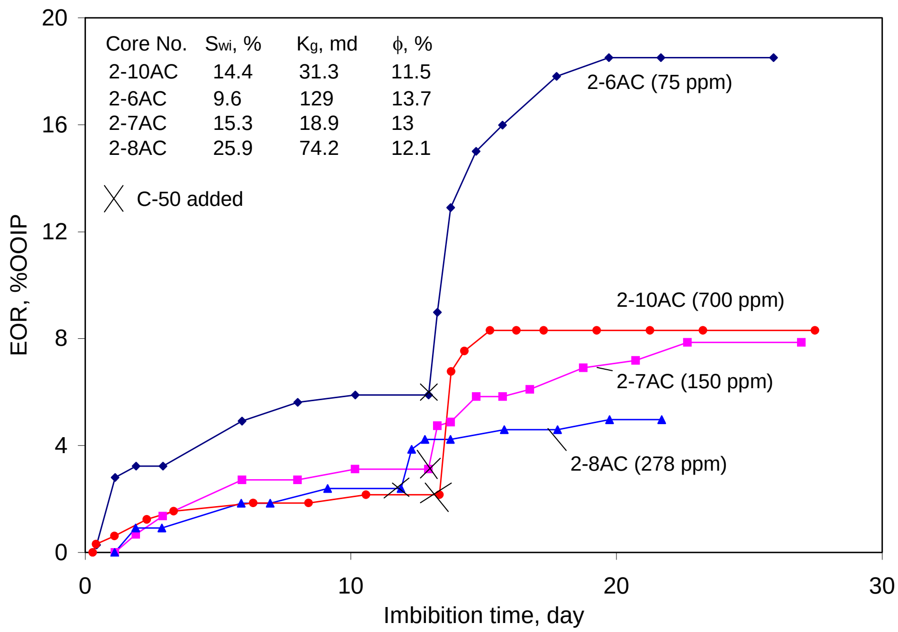


Fig. 2-2-3. The effect of C-50 concentration on Cottonwood oil recovery by imbibition from cores with 9.6–25.9% initial water saturation.

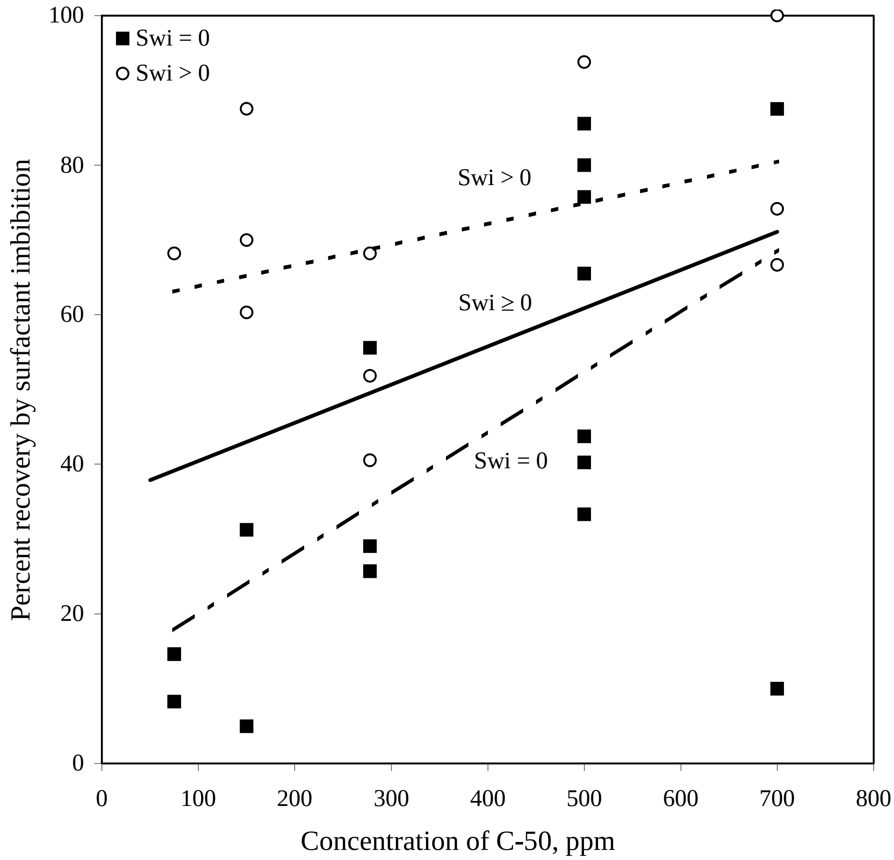


Fig. 2-2-4. The relationship of C-50 concentration versus oil recovery.

b. Presence of HCl: It is common practice in work-over treatments of wells to inject 15% HCl in order to remove corrosion products of iron (mainly iron sulfide) from the wellbore. In field tests related to this laboratory study, some of the wells were pretreated with HCl prior to surfactant injection. Laboratory tests of the effect of treatment with HCl solutions were made using acid concentrations of 0.5, 1.0, and 2.0 wt%. In all cases, HCl was added either shortly before (about 2–5 hours), or after the addition of C-50. The addition of HCl to the surfactant solutions did not significantly change the IFT between the solution and the crude oil. The laboratory tests showed that dilute acid solutions caused marked dissolution of the Cottonwood cores (Figs. 2-2-5 and 2-2-6). Production of CO_2 associated with the dissolution process drove oil from the rock as an emulsion. The combination of emulsion formation and rock dissolution made it difficult to assess changes in saturation accurately. After acid treatment, no recovery of oil was observed when cores were immersed in surfactant solutions, possibly because at least the outer volume of the rock became strongly water wet and any remaining oil was trapped (Fig. 2-2-7). The laboratory observations on the effect of acid treatment indicated that pre-treatment with acid could adversely affect oil recovery by imbibition of surfactant solution. For this reason, in the single well field tests of surfactant stimulation, some of the wells were not acidized prior to injection of surfactant solution.

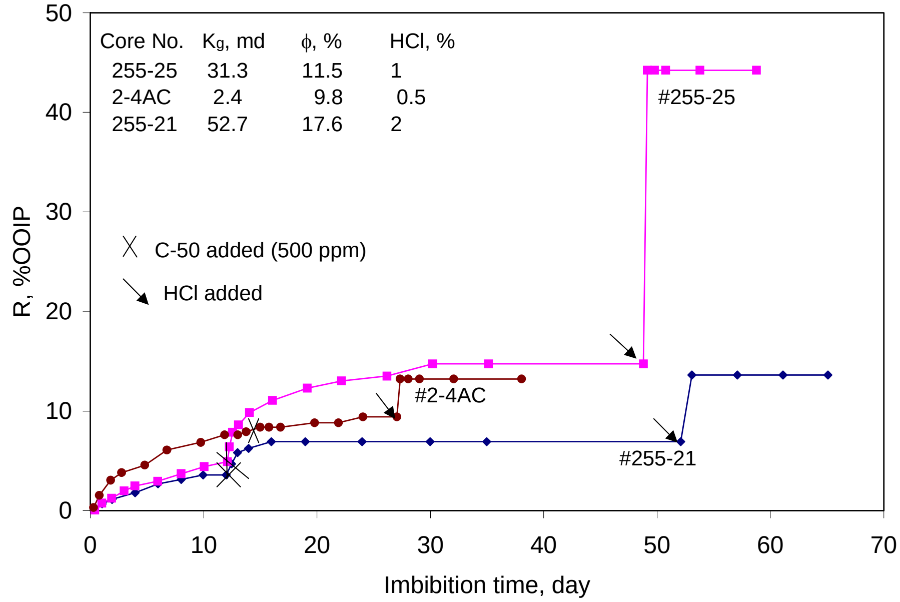


Fig. 2-2-5. The effect of HCl and C-50 on Cottonwood oil recovery.

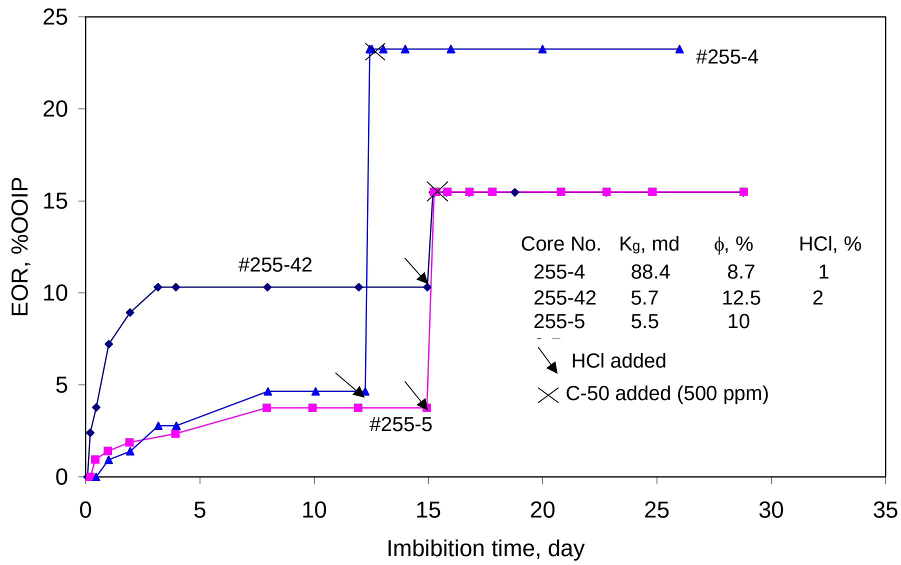


Fig. 2-2-6. The effect of HCl and C-50 on Cottonwood oil recovery.

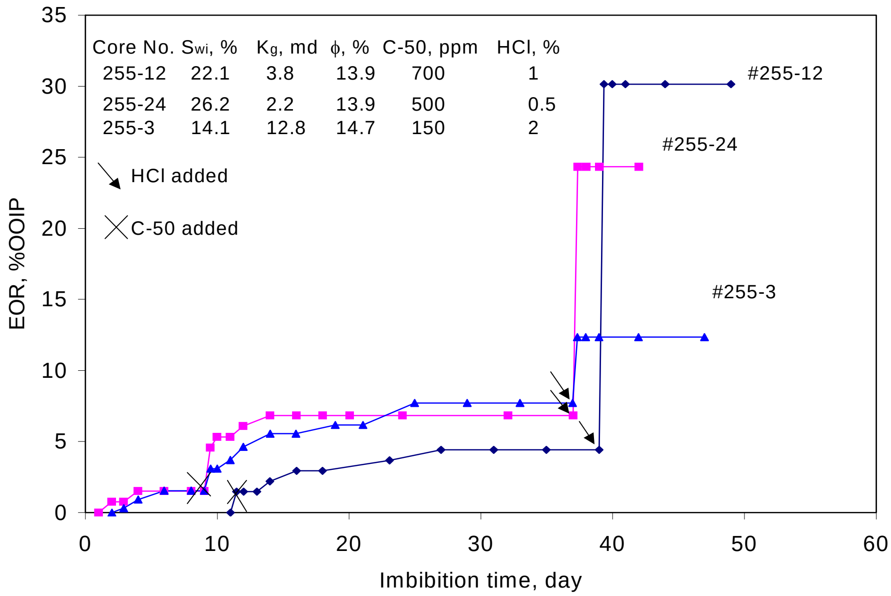


Fig. 2-2-7. The effect of HCl and C-50 on Cottonwood oil recovery with initial water.

Final enhanced oil recovery (EOR) versus bulk volume and AR is shown in Fig. 2-2-8 for all Cottonwood Creek cores without regard to the differences in treatment. Similar to results in Phase I and the results for the Yates cores, final imbibition oil recovery increased with porosity and the bulk volume of oil. Difference in permeability did not appear to affect the final oil recovery, but oil recovery decreased with increased aspect ratio, which is consistent with the Phase I and Yates results.

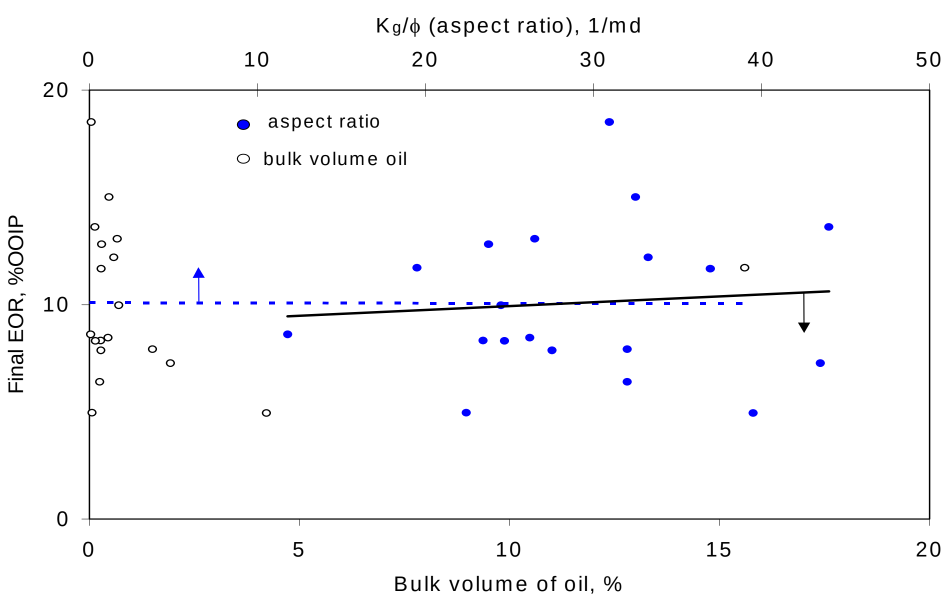
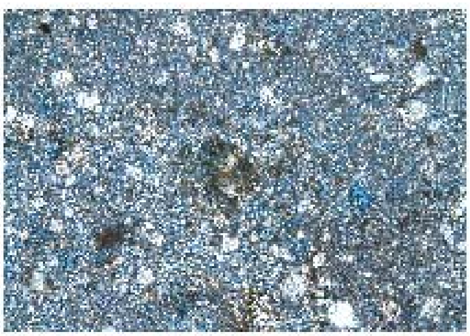


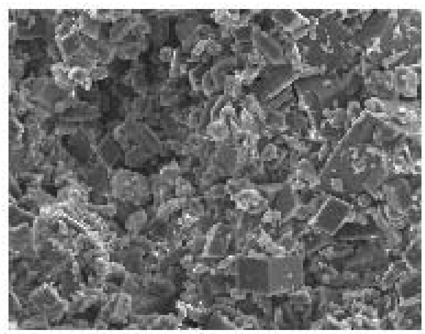
Fig. 2-2-8. Final recovery of Cottonwood oil as a function of BVO and AR.

Section 3. Lustre Oilfield

Lustre oilfield in Montana is a high-temperature carbonate reservoir and was identified in the Phase II proposal to be included in the laboratory testing procedure. Rock samples and crude oil from the Lustre oilfield in Montana were used to test a wide variety of surfactants in order to study the effect of surfactant on the imbibition oil recovery.

<u>Core samples:</u> 25 core plugs with a 1” (~ 2.5 cm) diameter from three Charles “C” formations at 5750 ft in the Lustre oilfield were acquired. The reservoir temperature was 170 °F (~ 86 °C). The reservoir rock was extremely tight and heterogeneous. It was difficult to observe individual crystals of dolomite by optical microscope from thin section slides. SEM pictures showed that the rock consisted of dolomite crystals, fossils, and very fine particles (Fig. 2-3-1). The air permeabilities ranged from less than 0.1 to about 4 md, and porosities ranged from about less than 1% to 25% (Table 2-3-1). These values were consistent with the porosity and permeability distribution of core values shown in Fig. 2-3-2.





(a) Thin section (1280 μ) (b) SEM (132 μ)

Fig. 2-3-1. Thin section and SEM pictures for Lustre rock.

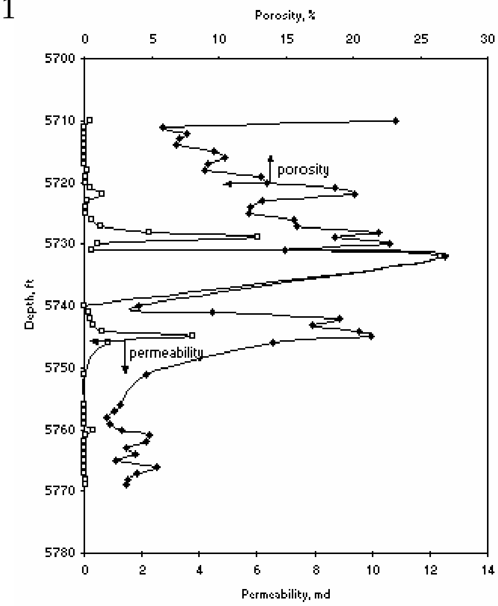
Table 2-3-1. Properties of Lustre cores						
Well name	**Core No.**	**L, cm**	**K_g, md**	**ϕ, %**	**Surfactant and concentration used,**	**IFT with Lustre oil, dynes/cm**
Core with S_{wi} = 0						
H. Beier #2	H25b	3.84	1.6	21.1	X100 (1 CMC) + A12-50 (0.5CMC)	2.2
	H26	3.92	1.3	17.4	X100 (1CMC) + A12-50 (1CMC)	2.1
	H27b	3.82	0.2	14.6	IMB-110 (2CMC)	6.4
	H28	3.78	3.2	25	5-70 PS (2CMC)	5.3
	H24b	3.96	0.9	20.8	AES 506 (2CMC)	9.1
	H25a	3.98	1.4	21.2	5-163 (2CMC)	16.9
	H20	3.96	1.2	19.2	AES 205 (2CMC)	5.4
	H27a	3.85	0.6	17.1	Witconate 3203 (2CMC)	3.9
	H23a	3.76	0.2	10.2	A12-50 (2CMC)	2.3
	H23b	3.74	4.0	23.2	T91-8 (2CMC)	5.1
	H22	3.83	0.04	7.3	C-50 (2CMC)	0.4
	H24a	3.79	0.3	13.4	X100 (2CMC)	5.6
	H37a	3.77	1.0	15.5	Witcolate 1276 (2CMC)	2.0
	H33	3.81	0.9	15.4	Witconate 3203 (1CMC) + A12-50 (1CMC)	0.06
	H29a	3.88	0.5	12.1	Witconate 3203 (1CMC)+ X100 (1CMC)	4.4
	H31b	3.8	0.3	11.9	Witconate 3203 (0.5CMC) + X100 (0.5CMC)	7.9
Bellonger Clark #2	BCa	3.6	0.1	7.6	S-31-T, 0.02 wt%	23.9
	BCb	3.9	0.6	16.4	SC-900, 0.02 wt%	24.9
	BCc	4.26	1.4	14.2	Witconate 3203(0.5CMC)+ A12-50 (0.5CMC)	0.07
Olfert #2	OB2a	4.31	1.0	18	Witconate 3203 (0.5CMC) + A12-50 (0.25CMC)	0.3
	OB2b	4.35	1.0	18.9	NCL-100, 0.02 wt%	0.3
Cores with S_{wi} > 0						
H. Beier #2	H32b	3.91	3.9	17.7	C-50 (2CMC), S_{wi} = 41.8%	1.6
	H34b	3.8	23.7	28.8	Witcolate 1276 (2CMC), S_{wi} = 29.3%	2
	H35a	3.77	15.5	27.6	T91-8 (2CMC), S_{wi} = 16.4%	5.1
	H36a	3.88	8.3	24.6	X100 (1CMC)+ A12-50 (1CMC), S_{wi} = 47.2%	2.1
B. Clark #2	BCd	3.6	4.6	21.8	X100 (2CMC), S_{wi} = 38.6%	5.6

Lustre oil: According to the information provided by Core Laboratories, the density of the Lustre oil was 0.8366 g/cc at 20 °C. The viscosity of the oil was 4.05 cp at 25 °C. The asphaltene content by using pentane as the precipitant was 0.24%. The acid number was 0.21 mgKOH/g.

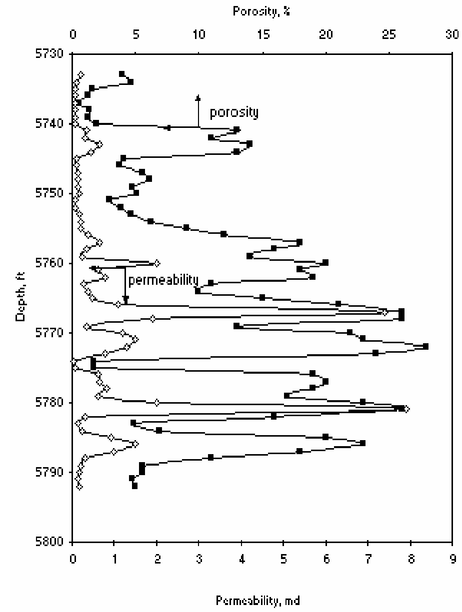
Lustre reservoir brine and laboratory brine: The reservoir brine composition according to the field data from Charles "C" formation was extremely concentrated. Attempts to prepare a brine composition corresponding to the field data were unsuccessful because of incomplete dissolution (or precipitation) of salts. In the laboratory, a modified brine (bicarbonate was excluded and sulfate concentration reduced), referred to as Lustre synthetic brine (LSB), was prepared (see Table 2-3-2). The IFT of LSB with Lustre crude oil was 23.9 dynes/cm measured by the drop volume method.

Surfactant solutions: A total of 21 different surfactants and mixture of surfactants were used in the imbibition tests for core samples from the Lustre oilfield (Table 2-3-1).

Except for the surfactant mixtures, all the individual surfactant solutions were made by adding a concentration of 2 CMCs of surfactant in the LSB. The IFTs are listed in Table 2-3-1



(a) Well Bellonger Clark#3



(b) Well H. Beier #B-3

Fig. 2-3-2. Core porosity-permeability distribution for two wells.

Table 2-3-2. Brine composition		
Composition	**Lustre brine, g/L**	**LSB, g/L**
Na+	60.659	2.648
Ca++	30.862	0.741
Mg++	2.440	0.085
CI-	154.84	4.901
HCO3-	0.415	0
SO4--	0.361	1.014
Total TDS, g/L	220,255	9.389

<u>Procedure:</u>

a) Gas permeability measurement: Gas permeability was measured with nitrogen for each dry core using Hassler core holders.

b) Porosity measurement: Some of the cores were saturated with Lustre crude oil directly by vacuum, and others were saturated with LSB. Porosity was measured from the increase in weight.

c) Establishment of initial water saturation S_{wi}: For cores saturated with LSB, the porous plate technique was used to decrease the water saturation. After drainage of the brine, the cores were evacuated and then saturated with Lustre crude oil. Since the Lustre core samples were extremely tight, it was sometimes very difficult to establish low initial water saturations. The porous plate technique was more effective in this regard than use of crude oil flooding.

d) Aging: The cores were then immersed in crude oil in aging cells. All cores were aged for 10 days at 70 °C.

e) Imbibition test: After aging, each aged core was submerged in LSB in an imbibition cell. All imbibition tests were performed at reservoir temperature (70 °C). Oil recovery by imbibition versus time was recorded. Most cores stopped producing oil by imbibition of synthetic brine within 7 days, or about 7–10 days. The cores were then immersed in surfactant solutions, and measurements of oil recovery versus time were continued.

f) Continuation of the spontaneous imbibition test: The cores were then transferred from surfactant solutions back to LSB. This process was designed to simulate the situation when surfactant was adsorbed by the formation.

<u>Test Results:</u> For all the cores with $S_{wi} = 0$, the oil recoveries from LSB imbibition reached between 17–50% of OOIP. For the cores with S_{wi} in the range of 16–48%, the oil recoveries for LSB imbibition were only 3–13%.

To verify the water-wetness of the Lustre cores before being soaked in surfactant solutions, dimensionless imbibition time versus oil recovery was compared with the strongly water-wet curve (Fig. 2-3-3). Ma et al. (1997) introduced the dimensionless imbibition time group. A surprising feature of this data is that the presence of initial water saturation (cores H32b and H35) appeared to inhibit imbibition of brine. Recovery (about 3%) from the cores containing initial water saturation was much less than for cores that did not contain initial water. In previous studies, the imbibition rate for mixed-wet sandstones increased systematically with an increase in initial water saturation in the range of 8–30% (Xie and Morrow, 2001). However, the mixed wettability states were generated in very strongly water-wet sandstone rather than as-received reservoir cores. Other examples showed that recovery (% OOIP) by imbibition of brine for the initially oil-saturated cores was higher than observed for any of the other dolomite rocks used in this study. A second surprising behaviour with respect to recovery for Cottonwood and Dagger Draw is that none of the Lustre cores responded to surfactant. These results demonstrate the need to test the response of individual crude oil/brine/rock combinations to assess the prospects for improved oil recovery.

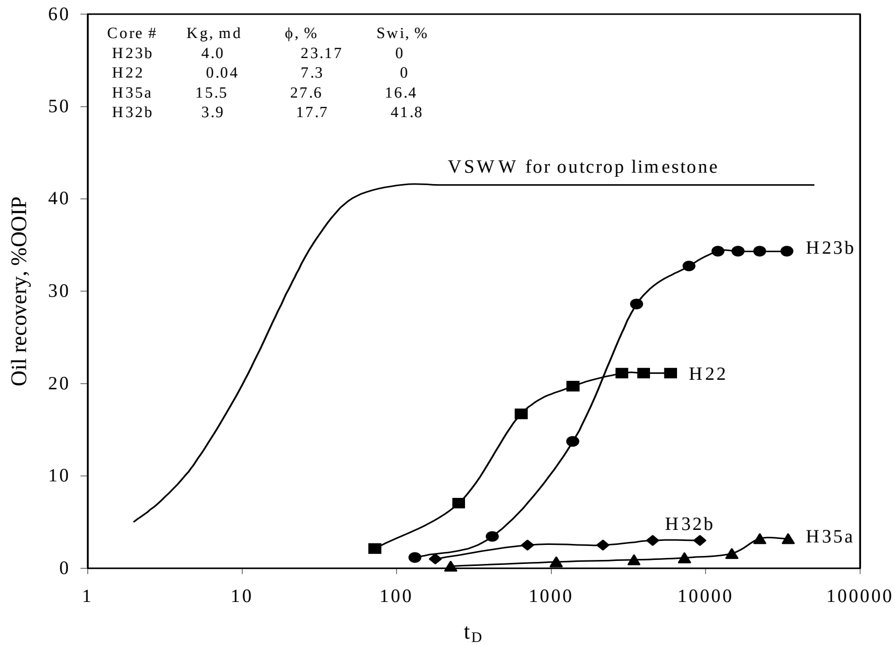


Fig. 2-3-3. Comparison of scaled imbibition curves with very strongly water-wet case.

Oil saturated cores: All the imbibition curves including brine imbibition and surfactant imbibition were plotted in Figs. 2-3-4 to 2-3-8. Some cores were soaked in surfactant solution for over 15 days, and some cores were transferred back into the brine after surfactant soaking for 15 days. No oil recovery increase was observed. The water-wet cores exhibited very high brine imbibition oil recovery. None of the chemicals had any effect on oil recovery either by altering wettability to promote imbibition or by gravity drainage. This indicated that improved oil recovery by imbibition of dilute surfactant solutions is dependent on the original wetting state of the rock. The initial oil recovery by spontaneous imbibition of brine was high.

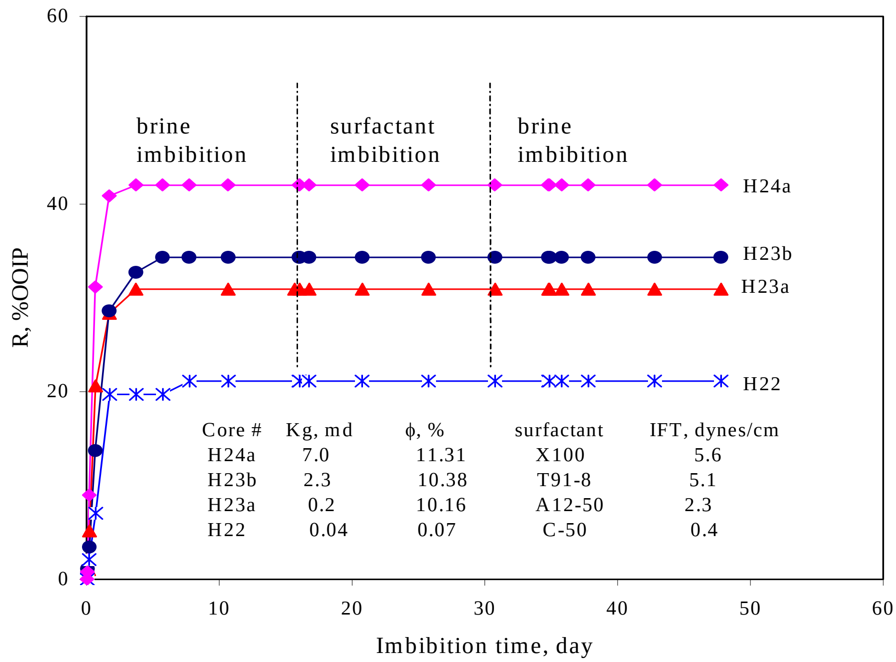


Fig. 2-3-4. Oil recovery from Lustre oil/brine/rock by spontaneous imbibition of brine followed by sequential immersion in either cationic or nonionic surfactant solutions.

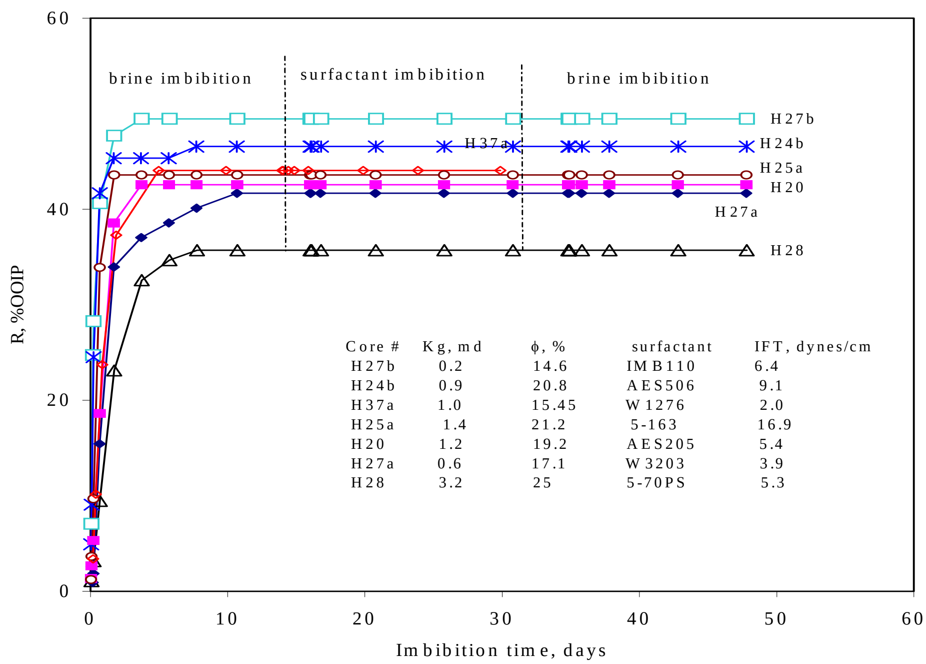


Fig. 2-3-5. Oil recovery from Lustre oil/brine/rock by spontaneous imbibition of brine followed by sequential immersion in anionic surfactant solutions.

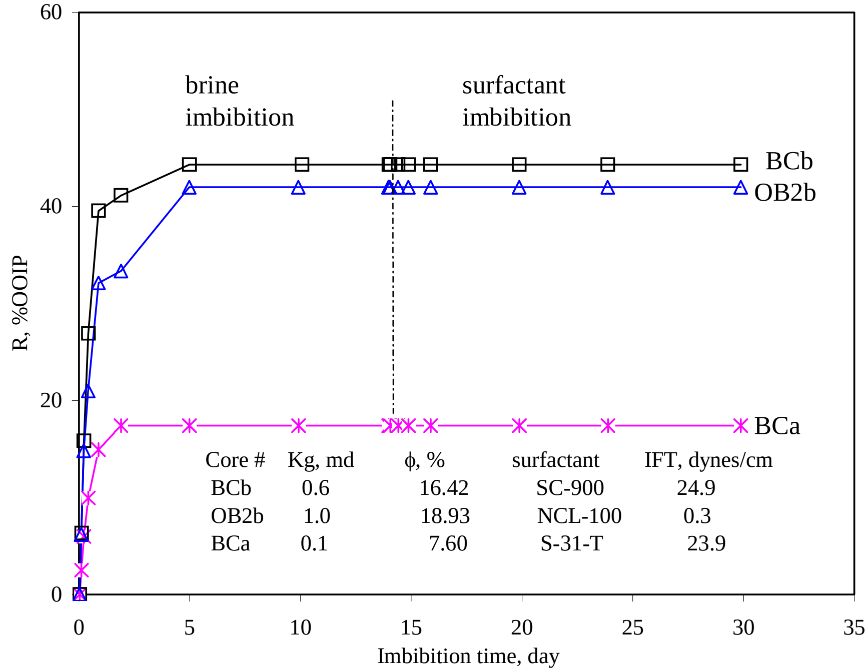


Fig. 2-3-6. Oil recovery by spontaneous imbibition for Lustre oil/brine/rock followed by immersion in surfactant solution.

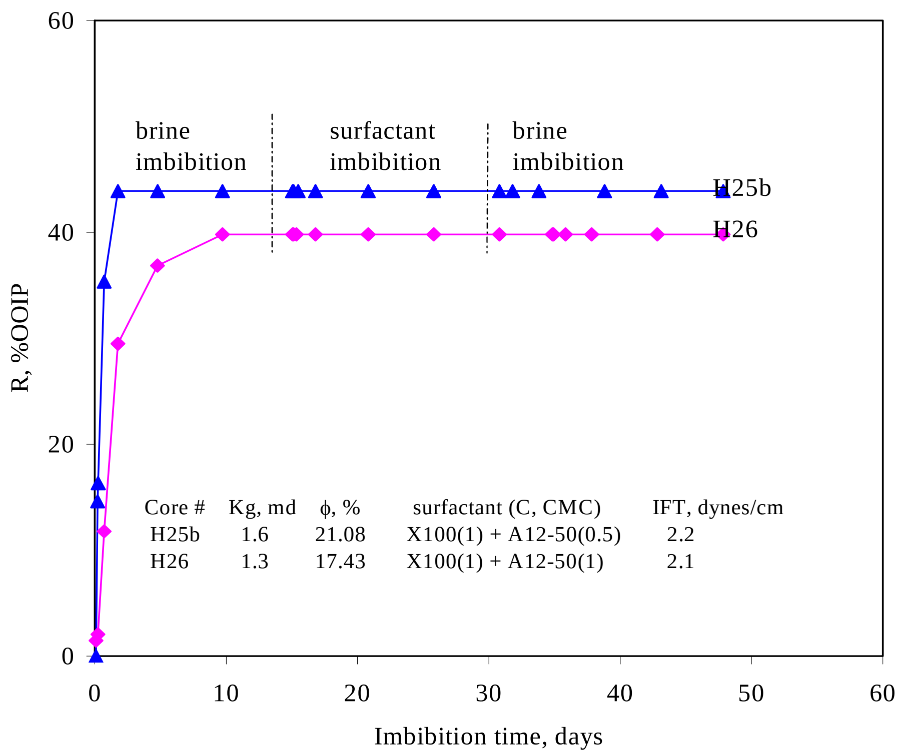


Fig. 2-3-7. Oil recovery by spontaneous imbibition for Lustre oil/brine/rock followed by soaking in surfactant solution and then re-soaking in brine.

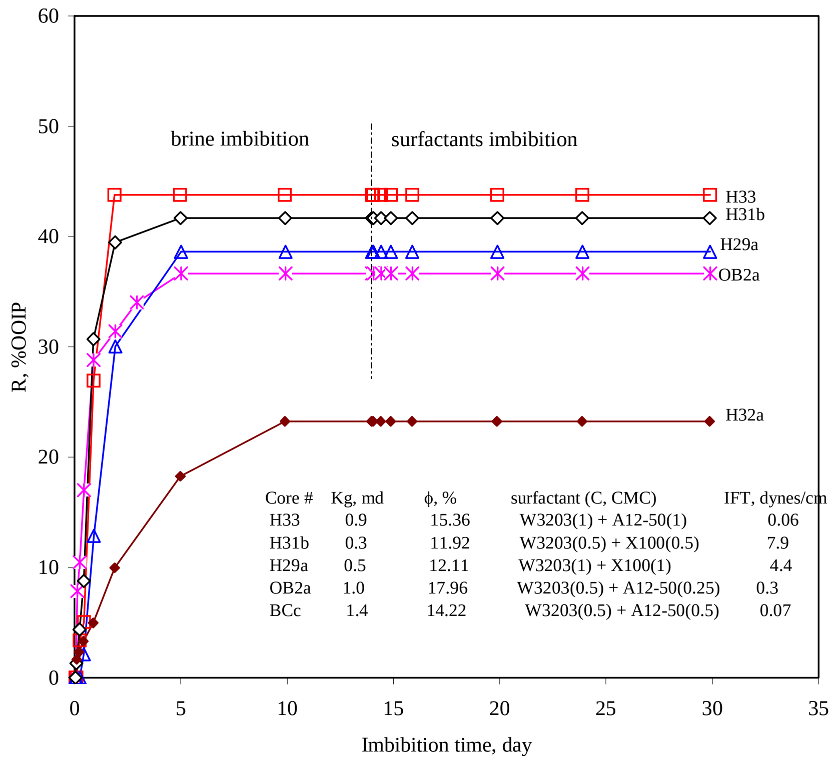


Fig. 2-3-8. Oil recovery by spontaneous imbibition for Lustre oil/brine/rock followed by immersion in solutions of mixtures of surfactants.

Cores with initial water saturation: As shown in Fig. 2-3-9, only 3–13% of OOIP was recovered after LSB imbibition into cores containing initial water saturation. This was much lower than the average oil recovery from cores that did not contain initial water. After the cores had been soaked in the surfactant solutions for over 10 days, only the surfactant mixture X100 + A12-50 had a positive, but very small, effect on oil recovery (increased 1.2%). The other surfactants did not affect oil recovery. It is worth noting that the Lustre rock was a combination of dolomite crystals, fossils, and very fine particles. Low-concentration surfactants may have been consumed by adsorption. Further, a high-surfactant concentration test would be necessary to evaluate the feasibility of surfactant treatment.

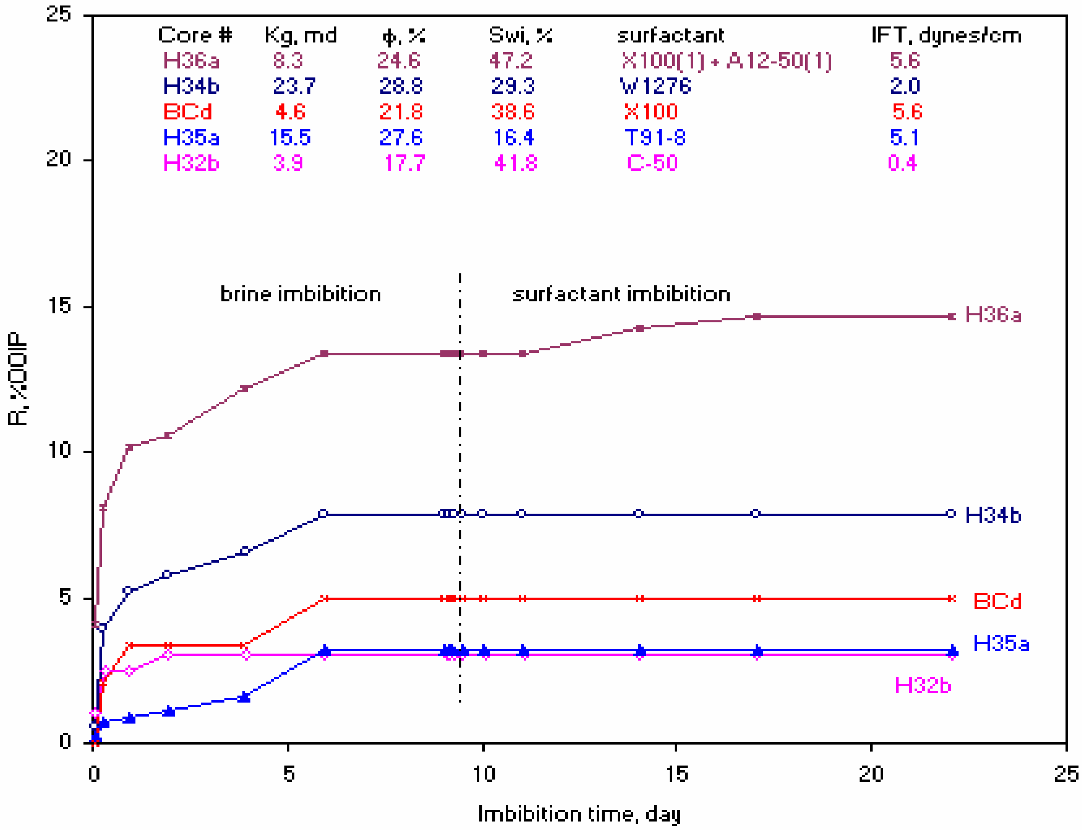


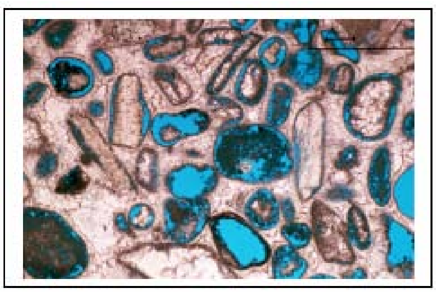
Fig. 2-3-9. Oil recovery by spontaneous imbibition for Lustre oil/brine/rock followed by immersion in various surfactant solutions.

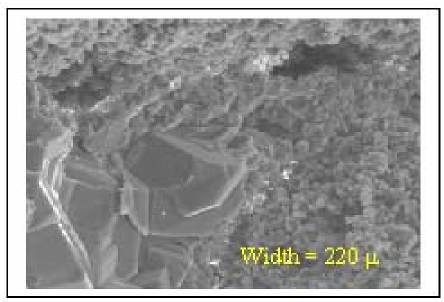
Section 4. Outcrop Carbonate Rock

The use of outcrop rock was intended to avoid the availability limitation of reservoir rocks. Outcrop rock was also a vehicle in which to study the responses of spontaneous imbibition oil recovery to surfactant treatment. Cationic surfactant C-50; anionic surfactants 5-67PS, 5-69PS, and 5-70PS; and nonionic surfactants T91-8 and X100 were added in the brine. The concentration of the surfactants is shown in Table 2-4-1. The test temperature was 60 °C.

Cores: The core plugs (1.5” in diameter) were cut from commercially supplied outcrop carbonate rock, a limestone named West Texas Creme. The porosity ranged from 15–26%, and the permeability ranged from 1.2–19 md (Table 2-4-1). Pictures of the thin section and SEM are shown in Fig. 2-4-1. Most of visible pores in the West Texas Creme sample are lined by tiny calcite crystals, with a few pores surrounded by coarse, sparitic calcite.

Table 2-4-1. Properties of outcrop cores							
Core No.	**L, cm**	**K_g, md**	**ϕ, %**	**S_{wi}, %**	**Surfactant & concentration, ppm**	**AR = ϕ/k_g, md^{-1}**	**BVO = $\phi(100-S_{wi})$**
Ct2a	7.7	5.9	20.5	17.4	X100, 400	3.48	16.93
Ct6a	7.4	10.3	23.1	18.5	T91-8, 450	2.24	18.83
Ct6b	7.4	10.6	22.6	17.2	C-50, 500	2.13	18.71
Ct7b	7.8	6.2	20.4	13.1	X100, 200	3.29	17.73
Ct10a	7.5	7.8	21.4	12.6	X100, 200	2.74	18.70
Ct11a	7.5	6.7	21.7	10.2	5-67PS, 150	3.24	19.49
Ct11b	7.6	6.1	21.6	15.1	5-70PS, 150	3.54	18.34
Ct13b	7.8	3.0	18.7	0.0	5-70PS, 150	6.23	18.7
Ct29a	7.7	2.9	18.1		C-50, 500	6.24	18.1
Ct32a	7.8	3.3	17.6		C-50, 500	5.33	17.6
Ct32b	7.3	4.3	20.1		5-67PS, 150	4.67	20.1
Ct34a	8.1	2.6	17.1		T91-8, 450	6.58	17.1
Ct34b	7.7	1.8	15.5		X100, 200	8.61	15.5
Ct36a	7.9	1.2	15.6		X100, 400	13	15.6
Ct36b	7.6	3.4	18.6		5-69PS, 150	5.47	18.6





(a) Thin section (~ 2000 μ)　　　(b) SEM picture

Fig. 2-4-1. Thin section and SEM pictures for outcrop limestone.

Oil and brine: Because of the abundant supply, Cottonwood crude was used in the outcrop carbonate rock. Cottonwood lab brine was used as the brine phase. The properties of the oil and brine are shown in Section 2, Cottonwood Creek Oilfield.

Interfacial tension: The IFT for the crude oil and reformulated brine was measured by the du Nouy ring method. The IFTs for the crude oil and surfactant solutions were measured by the drop volume method or the spinning drop method. All of the IFT data are included in Table 2-4-2.

Table 2-4-2. Interfacial tensions of the lab brine and Cottonwood oil

Lab brine	Concentration, ppm	Equivalent concentration of commercially supplied, lb/bbl	IFT at ambient temp., dynes/cm
No surfactant	0	0	31.96
C-50	500	0.36	0.16
T91-8	450	0.17	7.2
	750	0.27	5.7
X-100	200	0.072	6.2
	400	0.15	4.1
	6.24 wt% (0.1 mol)	22.55	0.5
5-67PS	150	0.11	6.1
5-69PS	150	0.21	7.0
5-70PS	150	0.18	4.9

Procedure:

*a) G*as *permeability measurement:* Air permeability was measured with nitrogen gas for cores using Hassler core holders.

b) Porosity measurement: All the cores were saturated with test brine by vacuum. Porosity was measured from the increase in weight. The cores were immersed in brine for 7–10 days to allow ionic equilibration.

c) Establishment of initial water saturation$_i$: Displacement of Cottonwood crude oil was used to establish initial water saturation, ranging from 0–18.5%.

d) Aging: The cores were then immersed in crude oil in aging cells. All of the cores were aged for 10 days at 60 °C.

e) Imbibition test: After aging, each aged core was submerged in lab brine in an imbibition cell. All imbibition tests were performed at Cottonwood Creek reservoir temperature (60 °C), and oil recovery by imbibition versus time was recorded. After brine imbibition, the cores were then immersed in surfactant solutions, and measurements of oil recovery versus time were continued.

Test results: Outcrop cores were tested with and without initial water saturations. There was significant oil recovery by brine imbibition: 30–60% OOIP, indicating strong water-wetness. Exposure to the surfactant solutions did not result in any significant additional oil recovery (Figs. 2-4-2, 2-4-3, and 2-4-4). Even C-50 and T91-8, which were shown to improve oil recovery for both Cottonwood and Dagger Draw cores, did not improve the oil recovery from outcrop cores. Pores in the West Texas Creme outcrop rock are lined with calcite, whereas pores in the two reservoir rock types (Cottonwood and Dagger Draw) are lined with dolomite crystals. Calcite has a much larger surface area, so that the surfactants might be consumed by adsorption. This is one possible reason for the difference in behavior between outcrop and reservoir rocks. Another reason is that reservoir carbonate rocks are notoriously difficult to clean, so the initial distribution of organic material in a dried (and cleaned) reservoir rock may differ significantly from the outcrop with respect to wetting behavior.

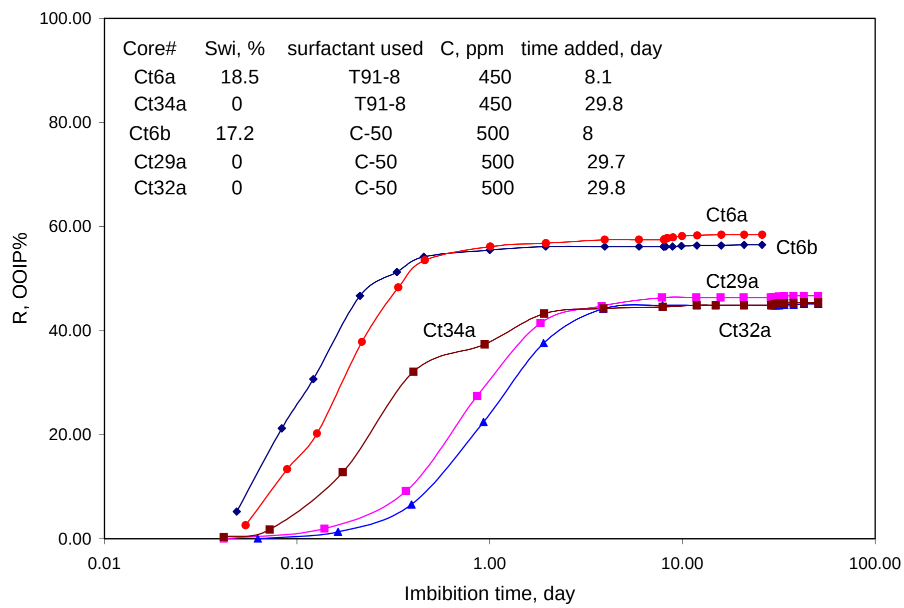


Fig. 2-4-2. The effect of cationic surfactant C-50 and nonionic surfactant T91-8 on oil recovery of outcrop cores.

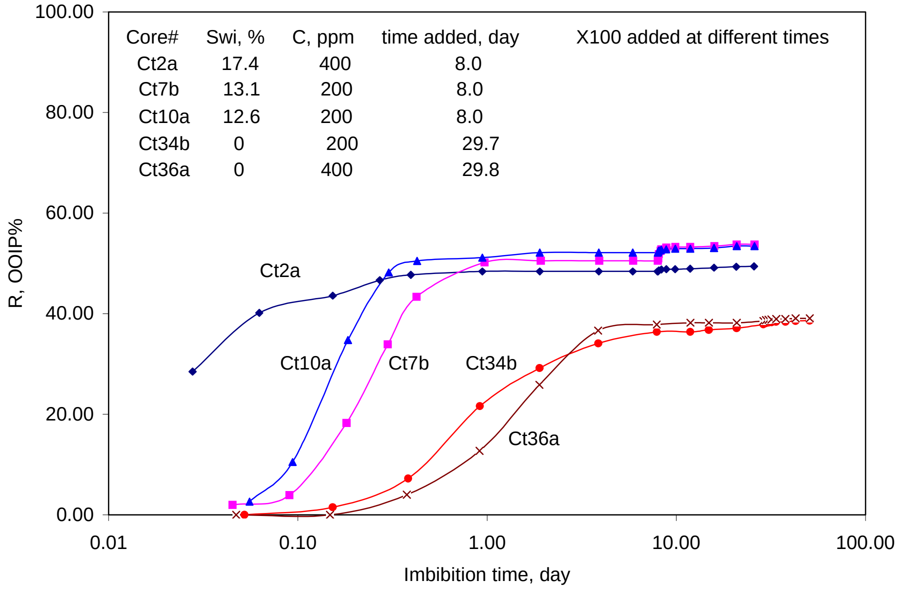


Fig. 2-4-3. The effect of nonionic surfactant Triton X100 on oil recovery of outcrop cores.

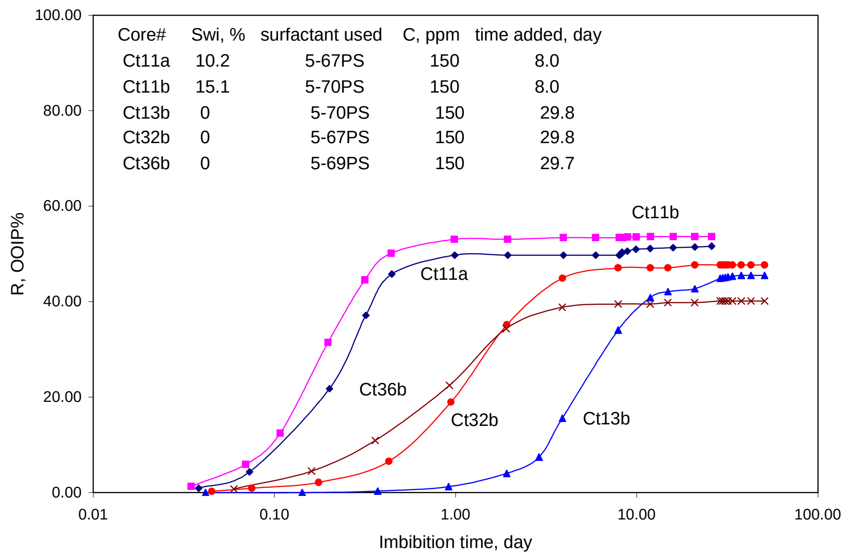


Fig. 2-4-4. The effect of anionic surfactants on oil recovery by imbibition of outcrop cores/Cottonwood oil.

Section 5. AI Analysis

Fuzzy ranking was applied to the cationic surfactant laboratory test results to identify the experimental parameters that most influence incremental oil recovery. The 18 core imbibition experiments without acid as shown in Table 2-2-1 and Fig. 2-2-2 were analyzed. The improved oil recovery is reported as EOR, percent primary or oil recovered with surfactant divided by oil recovery with brine (primary). Porosity, permeability, initial water saturation, and surfactant concentration as a function of EOR were evaluated for impact on recovery. The results are presented in Table 2-5-1.

Table 2-5-1. Results of laboratory core imbibition oil recovery				
Porosity %	Permeability md	Initial water saturation, %	Surfactant concentration, ppm	EOR, % primary
17.4	3.6	0.0	500	78
13.7	129.4	9.6	75	214
9.5	13.1	0.0	278	41
12.8	21	0.0	700	700
12.8	3.41	0.0	278	125
13.0	11.1	0.0	150	45
13.3	9.1	0.0	75	17
13.7	12.3	23.5	278	214
16.0	22.9	7.6	278	68
9.8	5.6	0.0	75	9.0
10.6	6.4	0.0	150	5.2
15.8	1.5	0.0	278	35
7.8	0.2	0.0	700	11
13.0	18.9	15.3	150	152
11.4	16.8	17.8	150	233
11.5	31.3	14.4	700	287
6.4	77.9	26.3	700	200
12.1	74.2	25.9	278	108

The fuzzy curves can be visually evaluated in Figs. 2-5-1 through 2-5-4.

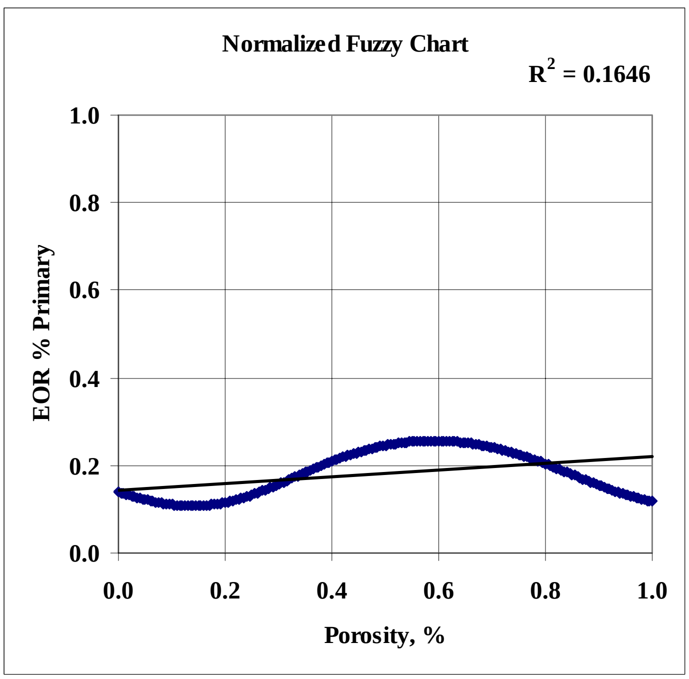


Fig. 2-5-1. Normalized fuzzy curve suggests little correlation between porosity and recovery.

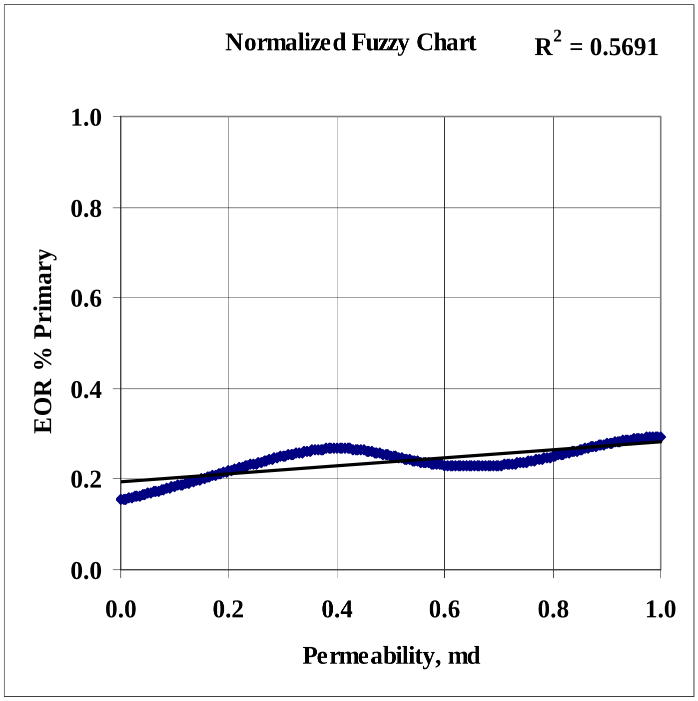


Fig. 2-5-2. Flat normalized fuzzy curve suggests a weak relationship between permeability and recovery.

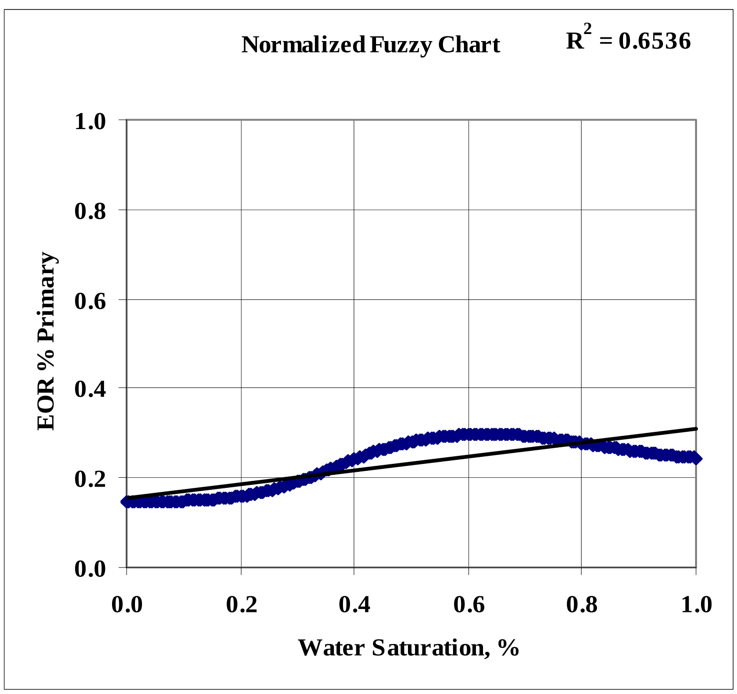


Fig. 2-5-3. Normalized fuzzy curve suggests little relationship between initial water saturation and recovery.

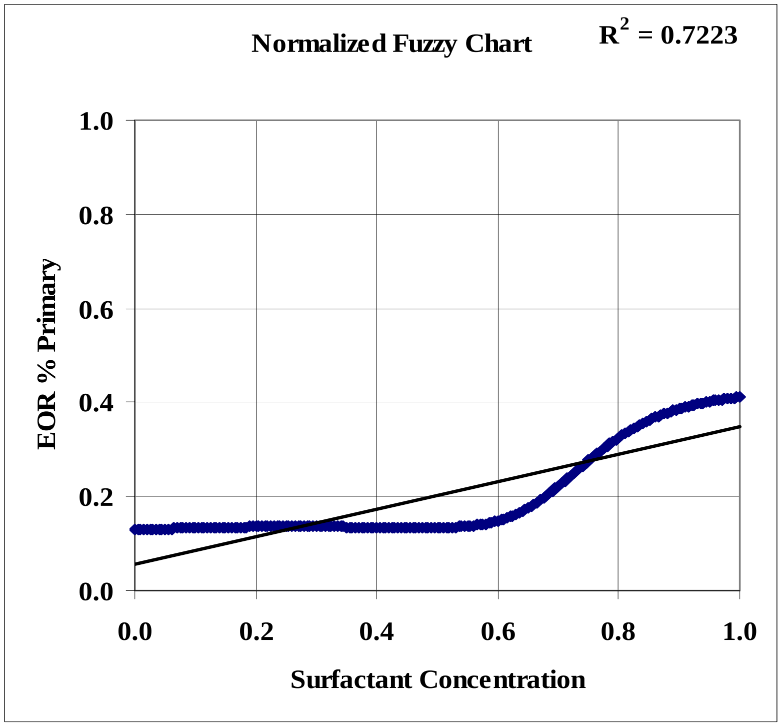


Fig. 2-5-4. Fuzzy curve suggests that a normalized surfactant concentration greater than 0.6 is necessary to affect oil recovery.

The normalized fuzzy curves suggest that of the four parameters surfactant concentration most affects the recovery results. Notice that a minimum surfactant concentration (0.6 normalized or ~450 ppm) is necessary to ensure spontaneous recovery if sufficient permeability is available.

Chapter 3. Laboratory Summary

Laboratory results show that the improved imbibition oil recovery technique with surfactants was effective for crude oil/brine/rock from the Cottonwood Creek and Dagger Draw oilfields but not for the Lustre oilfield and outcrop rock. A contributing factor may be the marked differences in mineralogy and pore structure of the rock samples from these reservoirs. Rocks from Cottonwood Creek and Dagger Draw oilfields are formed by dolomite crystals, while Lustre rock contains fossils and fine particles, and thus a much larger surface area. It was possible for the fine particles to adsorb the surfactant before it could alter the wettability. The imbibition results for outcrop limestone rock confirmed this hypothesis since limestone has a much larger surface area than that of dolomite. Another possible reason may be the different properties of the crude oil from these reservoirs. The wettability of Cottonwood Creek and Dagger Draw cores obtained by imbibition rates appeared very weakly water-wet, but some of the Lustre and outcrop cores appeared strongly or moderately water-wet.

The study of improved oil recovery by use of surfactants has been going on for over 40 years. Use of surfactants to alter the rock surface to more water-wet is a very important mechanism for EOR (Graham et al., 1957). Craig (1988) showed that surfactants can alter the rock surface from oil-wet to surfactant-wet, then oil can be displaced from the pores. Stone et al. (1970) improved oil recovery by altering the rock surface to oil-wet. Laboratory results in this report indicate that initial wettability in the range of weakly water-wet to oil-wet is needed for improved oil recovery by the use of surfactants in order to promote spontaneous imbibition. The success of the surfactant treatment may also depend on the pore structure and mineralogy.

As proposed in previous reports, the possible mechanisms of improved imbibition recovery for surfactant solutions in our work are as follows:

<u>Cationic surfactant</u>: Cationic ions interact with the adsorbed anionic materials from the crude oil, resulting in the release of the adsorbed organic materials from the rock surface. As the rock surface becomes more water-wet, the imbibition rate is increased (Standnes and Austad, 2000). The IFTs between the crude oil and the surfactant solutions are much lower than that of the crude oil and the synthetic brine.

<u>Nonionic surfactant</u>: The possible mechanism by which the nonionic surfactant T91-8 improved oil recovery is that T91-8 decreased the IFT between oil and brine by 4–5 times. The cationic surfactant reduced IFT by a factor of 30. The corresponding increase in the Bond number, $N_a = \rho g r^2 / \sigma$, probably contributed to improved oil recovery through gravity segregation (Chen et al., 2000).

If IFT is sufficiently low, then capillary pressure pc is also very small. According to the expression for pressure $p = p_c + \Delta\rho g h$, gravity segregation will only significantly contribute to oil recovery in cores if pc is very small.

<u>Anionic surfactant</u>: Anionic surfactants can also decrease the IFT and improve the gravity segregation. For carbonate rock surfaces, anionic surfactants can alter the wettability to more water-wet only if the brine pH is high, so that the rock surface appears negatively charged (Hirasaki and Zhang, 2003). However, it is very easy for precipitation to occur in carbonate reservoirs. Pores may become blocked with scale when the brine pH is

high. Therefore, use of high pH brines in field operation for carbonate reservoirs may cause operational problems.

Surfactant mixtures: The mixtures were usually made up with cationic and nonionic surfactants, anionic and nonionic surfactants, and cationic and anionic surfactants. Besides greatly decreasing the IFTs between oil and water, the surfactant mixtures may provide improved oil recovery mechanisms from the individual surfactants in the mixtures.

Chapter 4. Field Test

Section 1. Field Work

Surfactant soak treatments were performed on 24 producing wells in the Cottonwood Creek Phosphoria Unit for improved spontaneous imbibition oil recovery. The wells were selected based on production performance and casing integrity. The nonionic surfactant T91-8 in KCl brine solution was used in the field treatments. The area map shown in Fig. 4-1-1 locates the field in Wyoming.

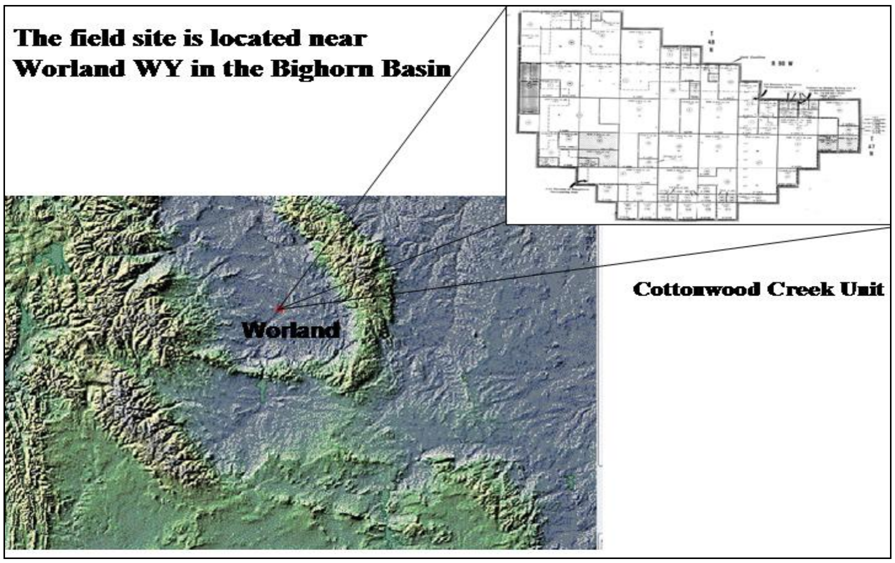


Fig. 4-1-1. Location of the Cottonwood Creek oilfield.

The location of the experimental test wells within the Unit is shown in Fig. 4-2-2.

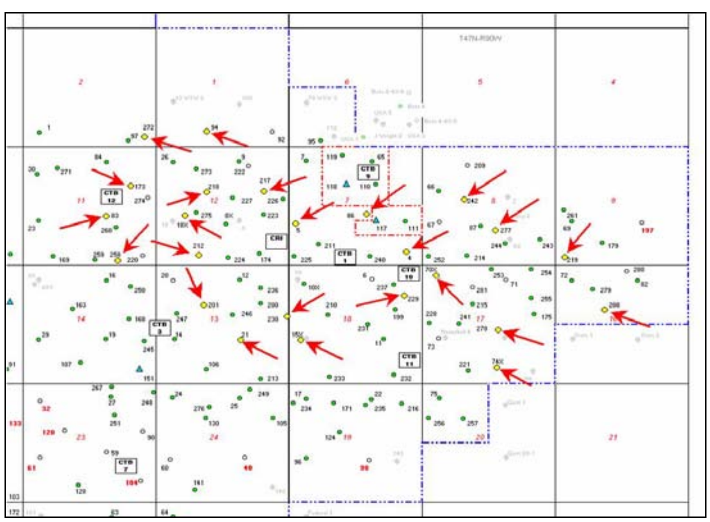


Fig. 4-1-2. Experimental well locations.

The experimental well database is shown in Table 4-1-1. The wells were assigned treatment volumes of 500, 1000, or 1500 bbl based on the minimum 0.02 bbl/ft^2 value and the square feet of fracture surface area. The surface area was calculated from the fracture half-length determined by pressure transient analyses.

Table 4-1-1. Surfactant soak test wells

	7-02 Production			Acid	Fracture	Proposed	Surfactant	GR-N	Core
Unit	Oil	Water	Gas	Wash	Surface	Treatment	Concentration	Logs	Analysis
Well No.	bbl/d	bbl/d	Mcf/d		Area, sq ft	bbl	ppm		
4	2.9	1.0	16.3	No	1532	1500	1500	Yes	
5	1.7	0.0	24.0	Yes	93	1000	750	Yes	Yes
21	3.7	7.8	15.9	Yes	93	1000	750	No	
83	3.4	0.0	75.7	No	29478	1500	1500	Yes	
86	1.0	0.7	1.4	No	8073	1500	1500	No	
94	3.7	2.6	7.0	Yes	40	1000	750	Yes	
173	3.4	0.0	17.8	Yes	44	1000	750	Yes	
201	2.5	5.1	14.8	Yes	120	1000	750	Yes	
208	11.1	1.7	39.9	Yes	13	500	750	Yes	
212	2.2	0.0	54.3	Yes	417	1500	1500	Yes	
217	1.3	3.5	38.5	Yes	228	1000	750	Yes	
218	6.8	1.0	86.1	No	1276	1500	1500	Yes	
219	0.0	0.0	4.0	Yes	233	1000	750	Yes	Yes
229	7.0	5.3	18.7	Yes	11	500	750	Yes	
230	3.9	2.0	38.5	No	915	1500	1500	Yes	Yes
242	4.4	1.7	19.2	Yes	156	1000	750	Yes/No	
258	4.2	2.0	77.2	No	807	1500	1500	Yes	Yes
272	5.9	0.0	19.3	Yes	3	500	750	Yes	
277	1.9	0.0	16.3	No	1671	1500	1500	Yes	Yes
278	4.1	3.9	48.7	Yes	9	500	750	Yes	Yes
15X	4.5	2.7	43.0	Yes	24	500	750	Yes	Yes
18X	0.0	0.0	0.0	Yes	7	500	750	Yes/No	Yes
70X	5.5	1.6	31.1	Yes	17	500	750	Yes/No	
74X	3.2	2.0	10.4	Yes	7	500	750	Yes	Yes

The surfactant concentration was either 750 or 1500 ppm depending on the presence or absence of an acid wash prior to the addition of surfactant. The acid wash was designed to clean iron sulfide-asphaltene sludge from the wellbore. The initial surfactant soak stimulation procedure is shown in Table 4-1-2. The xylene/HCl was found to be detrimental to the imbibition process and was later omitted.

Table 4-1-2. Surfactant treatment program–Cottonwood Creek Phosphoria Unit Washakie County, Wyoming	
1.	Inspect location & roads. Repair as needed for service equipment.
2.	RU H&P pump truck. Truck tank must be clean. Clean up wellbore as follows.
a.	Pump 150 gal xylene down casing. RD & shut-in well overnight.
b.	RU, mix & pump 1000 gal 15% HCl acid containing 1 gal of corrosion inhibitor, 1 gal of nonionic surfactant, & 20 gal of iron sequestering agent (acetic acid) down casing.
c.	Displace acid to perforations with clean 2% KCl water. RD equipment.
3.	Start well & pump test for 5 days. Report oil, water, & gas rates & fluid levels daily.
4.	RU frac tanks & piping (see **Table 4-4-1** for treatment volumes). <u>Ensure equipment is clean for treating chemicals.</u>
5.	Load tank(s) with 2% KCl water & mix in Tomadol 91-8 imbibition chemical at 15.75 gal per 500 bbl of water.
6.	Open casing valve & allow treating fluids to gravity feed down casing until frac tank is empty. Report frac tank volumes (level) daily to determine rate of injection.
7.	When treatment is completed (frac tank(s) is empty), close casing valve & shut-in well for 7 days. RD frac tanks & piping.
8.	Start well after 7-day shut-in period & pump test for 5 days. After that, test well at least once per week until effectiveness of treatment can be determined. For each test, report oil, water, & gas production & fluid level surveys. If the well pumps off, report run-time per 24- hour period.
9.	Final each procedure with approval from engineering or management.

The well experiments began in October 2002. A typical experimental system is shown in Fig. 4-1-3. The photo was taken during an inspection of the field. Three 400-bbl surfactant storage tanks and a water truck used to deliver the premixed 750- or 1500-ppm surfactant solution are shown. The surfactant was added to the annular space between the well casing and the tubing where it feeds into the formation by gravity.

Fig. 4-1-3. Inspection of typical surfactant soak experimental facility.

After 10 days of shut-in following the injection of the surfactant T91-8 at 750 ppm, production water samples were collected from a well (CCU 201) for four consecutive days. The IFT was measured in the laboratory by a drop-volume Kruss tensiometer DVT-10. The purpose was to estimate the concentration of surfactant in the produced fluid (Table 4-1-3). The improved oil recovery was not obvious. One can conclude that the injected surfactant was totally “consumed” by the formation, and the IFT of produced water was about that of original value. A higher surfactant concentration was needed to decrease the IFT. After analysis and discussion of the field test results by involved parties, a modified procedure (Table 4-1-3) was performed on the remaining eight wells.

Table 4-1-3. Interfacial tension for #CCU 201 produced brine and reservoir crude (22 °C)

Sample date	Original brine	11/18/02	11/19/02	11/20/02	11/21/02
IFT, dyne/cm	28.5	26.0	26.7	28.3	28.3

The schematic in Fig. 4-1-4 depicts the wellbore of a typical experimental well. Generally the rod pump was set below the perforations. Thus, the wellbore clean-up pretreatment (xylene/HCl iron sulfide) had access to the formation. The production rates before (July 2002 rate) and after the surfactant treatments are shown in Fig. 4-1-5.

CONTINENTAL RESOURCES, INC

WELL NAME:	Cottonwood Creek Phosphoria Unit No. 230	SPUD DATE:	9/28/95
LOCATION:	2236' FNL & 151' FEL	RIG REL:	10/29/95
SEC/TWN/RNG:	SENE Sec 13-T47N-R91W	COMP DATE:	11/8/95
COUNTY, ST:	Washakie County, Wyoming	FIELD:	Cottonwood Creek
WELL TYPE:	Oil	FORMATION:	Phosphoria
CRI WI:	GWI-91.1% NRI (Oil)-82.02%	LEASE NO:	WYW04643
SSI NUMBER:	111790	API NUMBER:	49-043-20766

	MCFD	BOPD	BWPD
IP:		84	73

SURFACE CASING DESIGN

NOM DIAMETER: 9-5/8"

LENGTH	GRADE	WT per FT
12 jts	CF850	36#

SET DEPTH: 525'
LEAD CEMENT: 125 sx CL-G
TAIL CEMENT: 180 sx CL-G

PRODUCTION CASING DESIGN

NOM DIAMETER: 5-1/2"

LENGTH	GRADE	WT per FT
160 jts	L-80	17#

Top to Bottom

SET DEPTH: 6828'
LEAD CEMENT: 360 sx CG 12.2 ppg 2.34 cf/sx
TAIL CEMENT: 250 sx CG 15.2 ppg 1.3 cf/sx
TOP OF CEMENT: 3460' BY: Calc

PERFORATIONS	FORMATION	SPF
6618-6672	Phosphoria	4

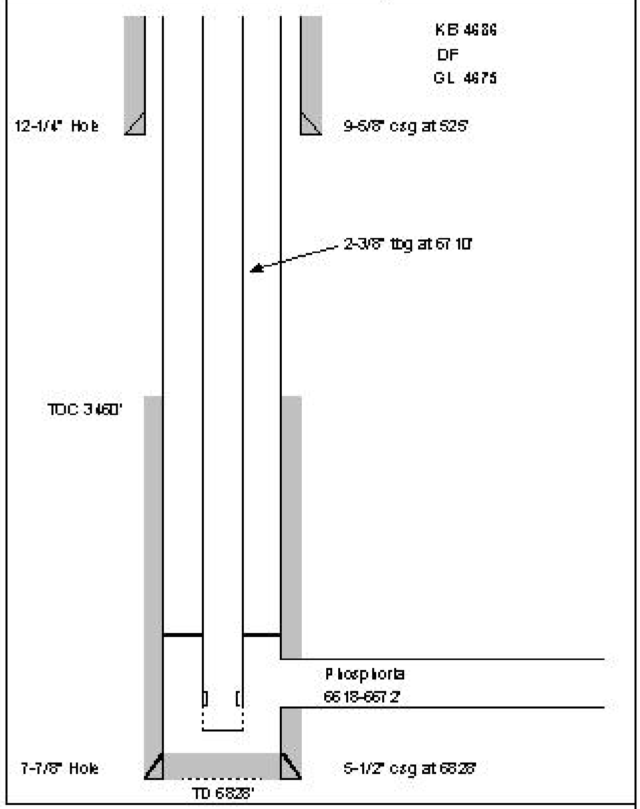
FORMATION TOPS:

FORMATION	TOP
Dinwoody	6556
Phosphoria	6598

TUBING STRING:

DESCRIPTION	SET DEPTH	
KB & Stretch	14	(11/25/99)
Tbg: 2-3/8" 4.7# L-80, 211 jts	6605	(11/25/99)
Baker TAC	6608	(11/25/99)
Tbg: 2-3/8" 4.7# L-80, 3 jts	6701	(11/25/99)
Seating Nipple	6702	(11/25/99)
Mud Anchor	6710	(11/25/99)
Polished Rod	26	(7/20/00)
7/8" x 6'-8' Rod Subs	40	(7/20/00)
Rods: 7/8" x 25', 100 jts	2540	(7/20/00)
Rods: 3/4" x 25', 118 jts	5490	(7/20/00)
Rods: 7/8" x 25', 48 jts	6690	(7/20/00)
Pump: 2" x 1-1/4" x 23' RHBC	6713	(7/20/00)

Cottonwood Creek Phosphoria Unit No. 230



STIMULATION: Initial Stimulation: 5000 gal 28% HCl, 6.7 BPM @ 2800#, ISIP - vacuum.
11/96: Acid Frac with 74760 gal SXE, 9996 gal 28% HCl, 97020 gal gelled wtr, 54 BPM @ 4200 psi, ISIP - 1175 psi.
11/97: Dump 3000 gal 15% HCl down annulus.
7/00: 1500 gal 20% HCl down annulus.

Fig. 4-1-4. Schematic of typical wellbore.

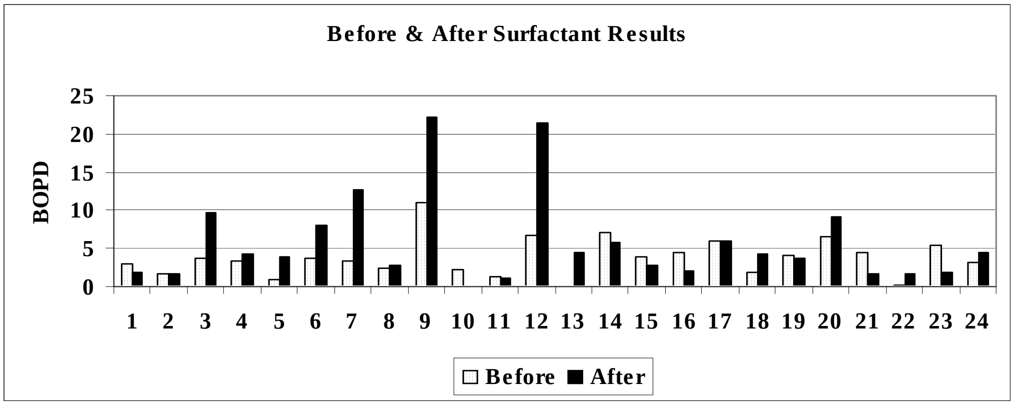


Fig. 4-1-5. Results of field trials.

The procedure outlined in Table 4-1-4 was used to treat eight wells once it was determined that acid was detrimental to the imbibition process.

Table 4-1-4. Surfactant treatment program modifications–Cottonwood Creek Phosphoria Unit Washakie County, Wyoming
1. Inspect location & roads. Repair as needed for service equipment.
2. Start well & pump test for 5 days. Report oil, water, & gas rates & fluid levels daily.
3. RU frac tanks & piping (see Table 4-4-1) for treatment volumes). <u>Ensure equipment is clean for treating chemicals.</u>
4. The treatment for the final eight wells in the program is being modified by increasing chemical concentration to 1500 ppm. The treatment total volume remains 1500 bbl. Load tank(s) with 2% KCl water & mix in Tomadol 91-8 imbibition chemical at 94.5 gal for 1500 bbl of water.
5. Shut down well for dump treatment. Shut-in flowline, open casing valve, & allow treating fluids to gravity feed down casing until frac tank is empty. Report frac tank volumes (level) daily to determine rate of injection.
6. When treatment is completed (frac tank(s) is empty), close casing valve & shut-in well for 7 days. RD frac tanks & piping.
7. Start well after 7-day shut-in period & pump test for 5 days. After that, test well at least once per week until effectiveness of treatment can be determined. For each test, report oil, water, & gas production & fluid level surveys. If the well pumps off, report run-time per 24-hour period.
8. Final each procedure with approval from engineering or management.

All experimental wells were treated between August 2002 and November 2003. The incremental oil shown in Fig. 4-1-5 is based on the oil rate reported to the State of New Mexico and the average of 6–10 well tests performed during the 30 days following the treatment. It is interesting to note that water production increased from all wells; thus, deliverability from all wells increased as a result of the surfactant soak treatments. Table 4-1-3 indicated that very little or no surfactant was left in the production brine, and, therefore, the formation wettability shifted away from oil-wet to water-wet. The absence of surfactant a few days after the treatment suggests that a change in the contact angle rather than the reduced IFT was the driving force. All wells were maintained in a pumped-off condition at all times.

Section 2. Analysis of Field Trials

Gamma ray logs were available for all wells in Table 4-1-1, and neutron logs were available for most wells. The neutron logs included neutron count rate (NCR) and neutron porosity logs. The NCR logs run during the early development of the field in the 1950s were converted to neutron porosity logs. The core data and the neutron count rate logs from well 71 were used to develop a conversion method. A plot of the log of the core porosity versus the NCR was constructed as shown in Fig. 4-2-1. Core measurements of 0.1% porosity or less are not included in the plot because the absolute values are not known. The laboratory equipment measured only values greater than 0.1 % porosity. The thick line to the left in Fig. 4-2-1 is a best-fit line to the core data points. The equation of this line ($y=676e^{-0.0174*NCR}$) was used to calculate a core porosity value for each NCR. The average of these values is considerably less than the 4.8% average of all core values. By trial and error, the intercept of the equation was increased from 676 to 1000 NCR. The thin line on the right is the line developed with 1000 intercept. The average of this dataset is 4.8% porosity.

The equation, $y = 1000e^{-0.0174*NCR}$, was used to estimate porosity values for wells with NCR logs. Statistical parameters of the porosity logs estimated in this manner were used as inputs to a neural network trained to predict the initial oil-producing rate.

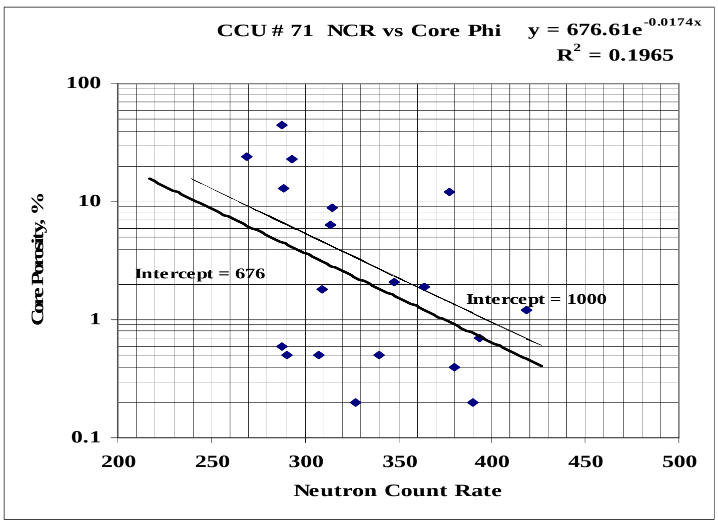


Fig. 4-2-1. Chart used to convert 1950s style neutron count rate logs to porosity.

The standard deviation of the statistical parameters and the average of the porosity logs through the pay interval were correlated with the average rate calculated from the first 12 producing months using a 2-3-1 neural network. The training results are shown in Fig. 4-2-2. Based on these results, it was expected that the porosity logs could be used to develop a direct correlation between laboratory oil recovery tests with cores and measured porosity, and incremental oil from the field test wells with porosity estimated from logs. The ability to correlate porosity logs with the initial oil production rate supported the use of logs to correlate with results of the surfactant soak treatment.

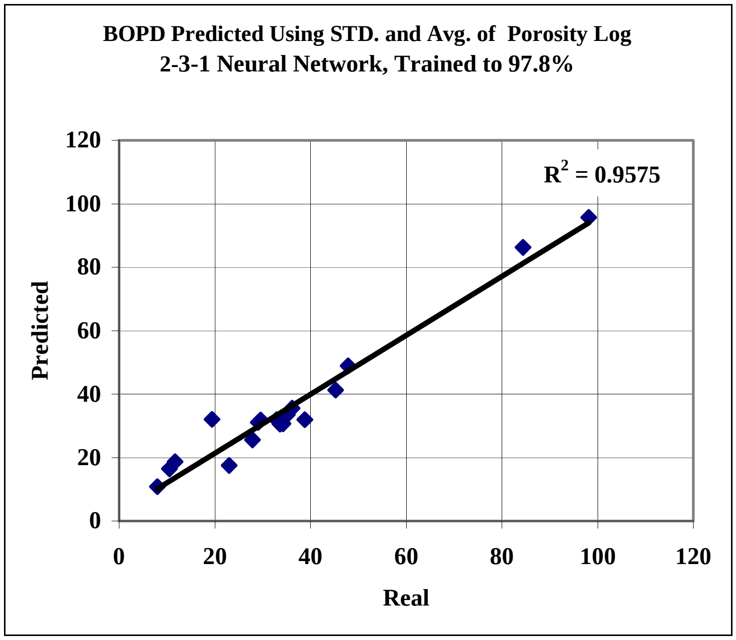


Fig. 4-2-2. Porosity log statistics used to predict initial oil rate, BOPD.

The use of statistics to describe log patterns is new. The concept is clarified in Fig. 4-2-3. Shown are gamma ray logs through two nearby wells in the same sandstone reservoir. Both intervals are about the same thickness. The well log on the left has a pattern that is smoother than the well log on the right. The jagged nature of the well on the right is expressed with its STD, 31.83, vs. the STD of 9.05 for the well on the left. The sum, average, and kurtosis are other statistical parameters that characterize patterns.

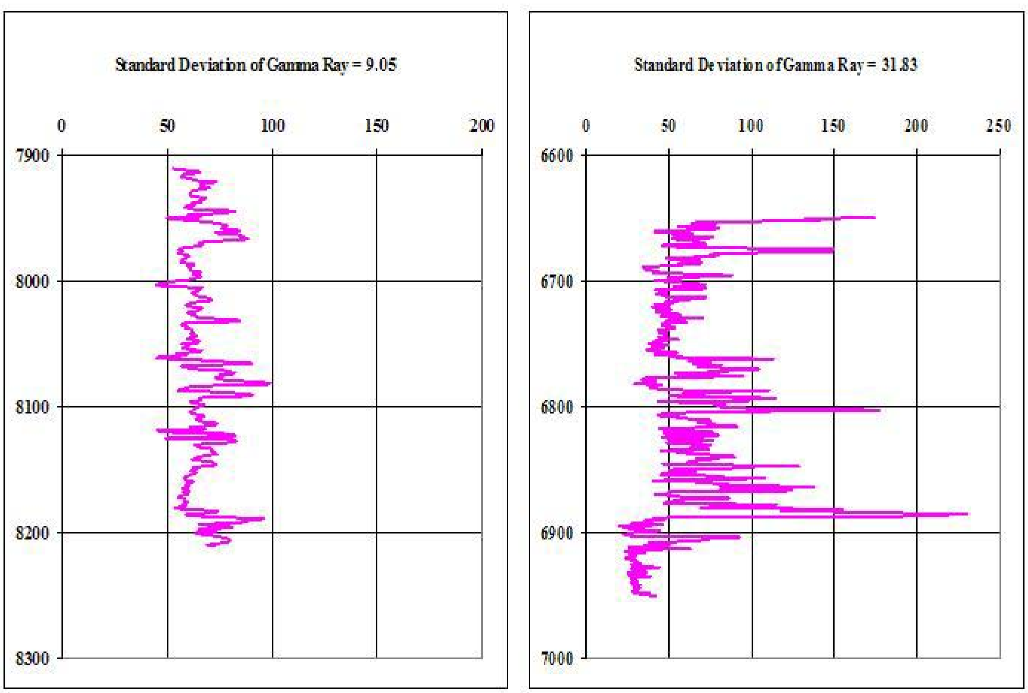


Fig. 4-2-3. Gamma ray log pattern represented by the standard deviation.

Section 3. Correlations

The 22 variables identified in Table 4-3-1 could have influenced the field results. Fuzzy curves were developed for these variables, and the results are included in Table 4-3-1.

Table 4-3-1. Field experimental variables (18 wells)				
No.	**Variable**	**R^2**	**Range**	**Goodness**
1	Standard deviation of gamma ray	0.97	0.39	1.36
2	Standard deviation of BVO log	0.85	0.52	1.36
3	Perforations gross thickness, ft	0.80	0.54	1.34
4	Total fluid (average over life of well), bbl/day	0.95	0.27	1.22
5	Water, bbl/day	0.93	0.25	1.18
6	Water cumulative, bbl	0.92	0.25	1.17
7	Total fluid cumulative, bbl	0.90	0.23	1.13
8	Oil cumulative, bbl	0.89	0.15	1.04
9	Kelly bushing elevation, ft	0.70	0.33	1.02
10	Water oil ratio, bbl/bbl	0.88	0.14	1.02
11	Sum of gamma ray	0.88	0.13	1.01
12	Oil, bbl/day	0.43	0.24	0.67
13	Average of neutron porosity	0.28	0.38	0.66
14	Total fluid, bbl /day	0.56	0.09	0.66
15	Phosphoria gross thickness, ft	0.07	0.52	0.58
16	Phosphoria bottom depth, ft	0.22	0.33	0.55
17	Perforations bottom depth, ft	0.17	0.36	0.53
18	Perforations top depth, ft	0.16	0.35	0.51
19	Phosphoria top, ft	0.15	0.33	0.48
20	Sum of neutron porosity	0.23	0.23	0.47
21	Average of gamma ray	0.06	0.24	0.30
22	Standard deviation of neutron porosity	0.01	0.18	0.20

As the size of the well treatment dataset grew from the 18 wells used to construct Table 4-3-1 to 21 wells, new fuzzy curves were developed. These curves ranked near the top the standard deviation of both the gamma ray and neutron logs and the average of the gamma ray log. Note that the average of the gamma ray and standard deviation of the neutron log are ranked at the bottom of the list of variables shown in Table 4-3-1, demonstrating the importance of the dataset domain when applying AI analysis.

The data from 21 of the 23 treated wells were sufficient to construct fuzzy curves of incremental oil as a function of the surfactant quantity expressed as pounds per foot of pay zone seen in Fig. 4-3-1 and as a function of barrels of surfactant solution used as shown in Fig. 4-3-2. The trend observed in Fig. 4-3-1 concurs with the laboratory observation that increased surfactant quantity increases the incremental oil.

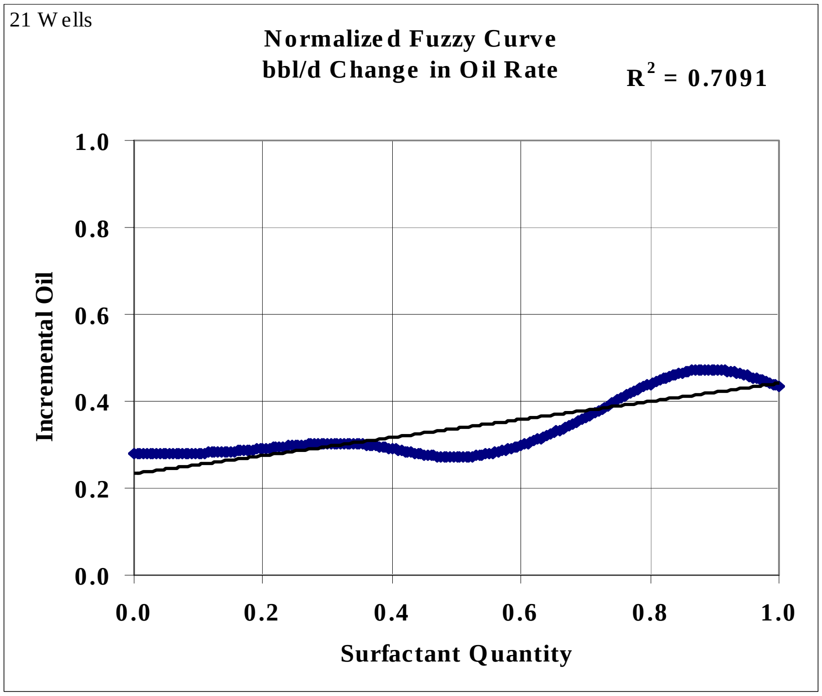


Fig. 4-3-1. Incremental oil vs. surfactant quantity.

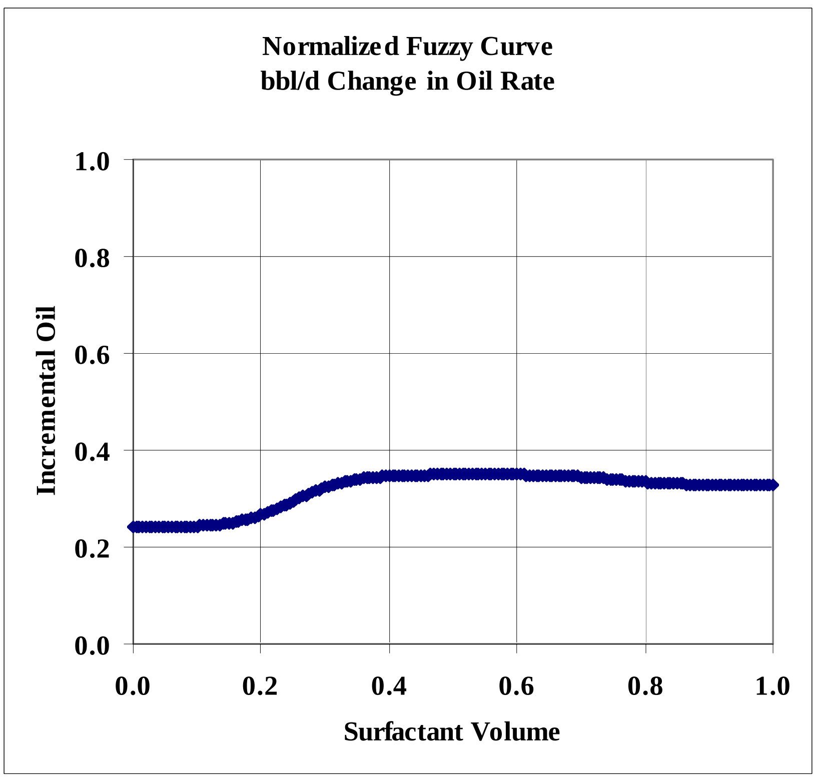


Fig. 4-3-2. Incremental oil vs. surfactant volume.

It is evident from the normalized curves that the volume of the surfactant used was less important than the quantity of surfactant used. A de-normalized Fig. 4-3-1 (not shown) indicates that a minimum of 20 lb/ft of surfactant is required.

Development of a neural network to predict a treatment result was restricted by the requirement that the network architecture be 10 weights or less. Thus, three inputs could have one hidden layer with two nodes (eight weights), or two inputs could have one hidden layer with two or three nodes (maximum nine weights). The statistical log attributes standard deviation, average, and sum were evaluated.

Recognizing that the log statistical variables average and standard deviation could have broad application, the variables were used as input to develop a neural network suitable for application design. A 3-2-1 neural network was trained with the standard deviation of the gamma ray and neutron logs plus the quantity in pound per foot of surfactant as the three inputs. The network trained to a correlation coefficient of 93% as shown in Fig. 4-3-3. This network produced the best validation tests. The tests consisted of parsing a single well during the network training and then predicting the known value.

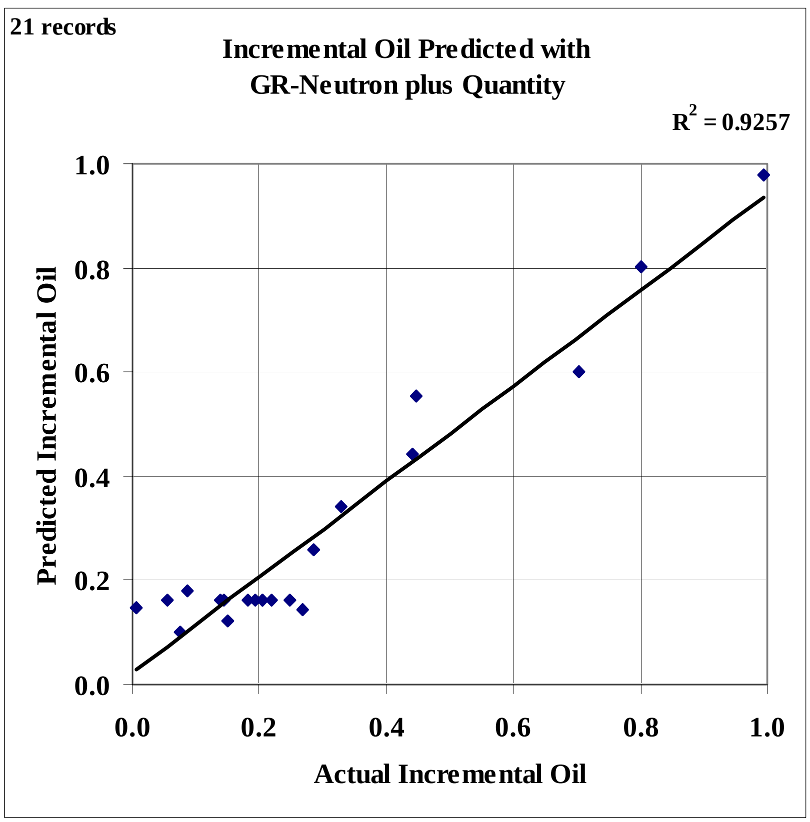


Fig. 4-3-3. A result from a three input (including quantity) neural network training.

A 3-2-1 neural network was trained with the standard deviation of the gamma ray and neutron logs plus the volume in bbl/ft of surfactant used as the three inputs. The network trained to a correlation coefficient of 94% as shown in Fig. 4-3-4.

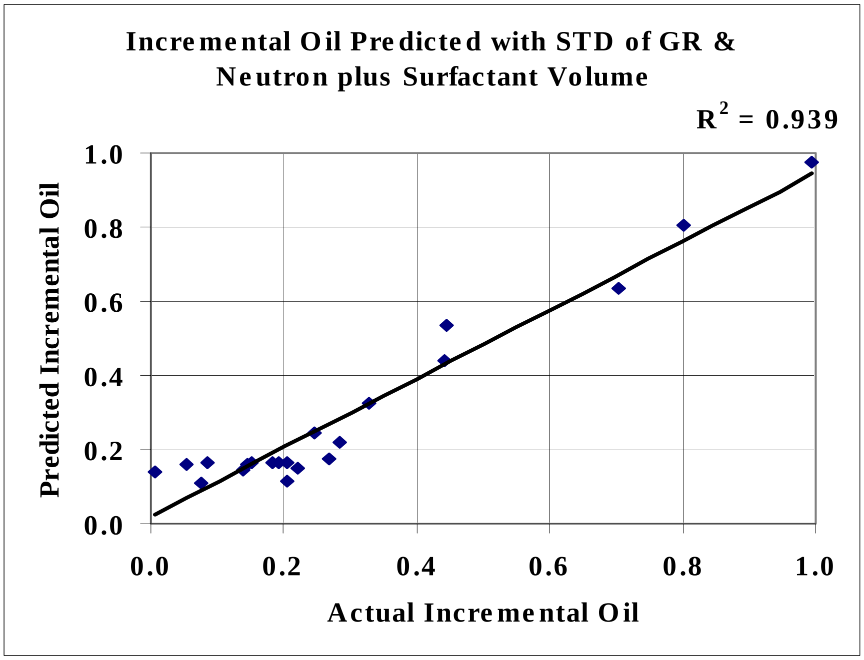


Fig. 4-3-4. A result from a three input (including volume) neural network training.

Recognizing that a gamma ray log is generally available for most wells, a 2-3-1 neural network was developed using only the gamma ray log and quantity of surfactant as inputs. The 92% correlation coefficient training result is shown in Fig. 4-3-5. The axes are de-normalized to show the actual and predicted oil rates in barrels oil per day.

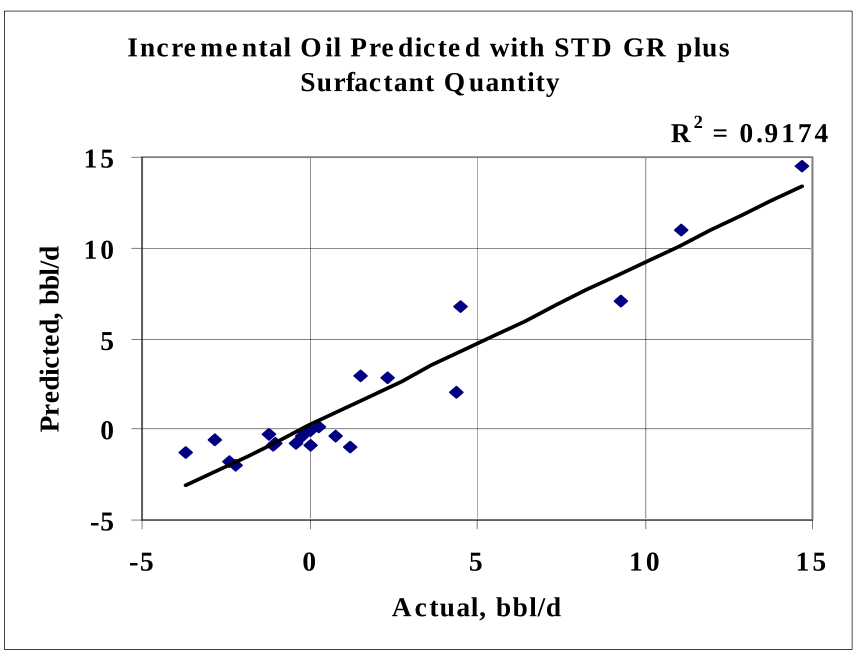


Fig. 4-3-5. Results from a two input (including surfactant quantity) neural network training.

The trained network was then used to estimate the amount of surfactant required to maximize the incremental oil. These results are shown in Table 4-3-2.

Table 4-3-2. Surfactant required to maximize incremental oil				
Well	**Actual quantity of surfactant lb/ft**	**Predicted quantity with GR & neutron logs lb/ft**	**Predicted quantity with GR logs alone lb/ft**	**Predicted incremental oil, bbl/d**
4	18	65	2000	14
5	5	25	25	15
83	14	35	175	15
94	5	25	2000	15
173	9	25	125	15
201	6	30	30	15
208	3	5	6	15
212	19	30	30	15
217	8	35	35	15
218	21	25	25	15
219	8	25	125	15
229	3	30	30	15
230	15	35	35	15
242	7	110	20000	14
272	3	45	45	15
277	17	40	2000	14
278	3	40	40	15
15X	5	35	35	15
18X	3	30	2000	14
70X	3	15	15	15
74X	3	15	15	15

The results shown in Table 4-3-2 demonstrate that inclusion of the neutron log with the gamma ray log to predict incremental oil generates different requirements for seven of the 21 wells. The economics of treating these seven wells (assuming only the gamma ray log is available for design purposes) are probably poor. The inclusion of the neutron log in the design brings valuable extra information. A dataset consisting of more than 50 wells would generate a more robust predictive tool.

Section 4. Economics

Several wells showed a marked increase in the oil rate as a result of the treatment, but 70% of the treatments were failures. Well 218 exhibited a positive response as shown in Figs. 4-4-1 and 4-4-2. The oil rate increased, and the oil cut decreased due to increased total fluid production. The oil rate versus cumulative oil curve indicates the estimated ultimate incremental oil recovery (EUIR) is 2500 bbl. All wells were analyzed in a similar manner. The average EUIR was 470 bbl for a sum of 9,800 bbl. The total cost to treat the first 19 wells was $157,000 ($8300/well) including acid and pulling unit cost. The cost of the surfactant treatment alone averaged $2500 per well.

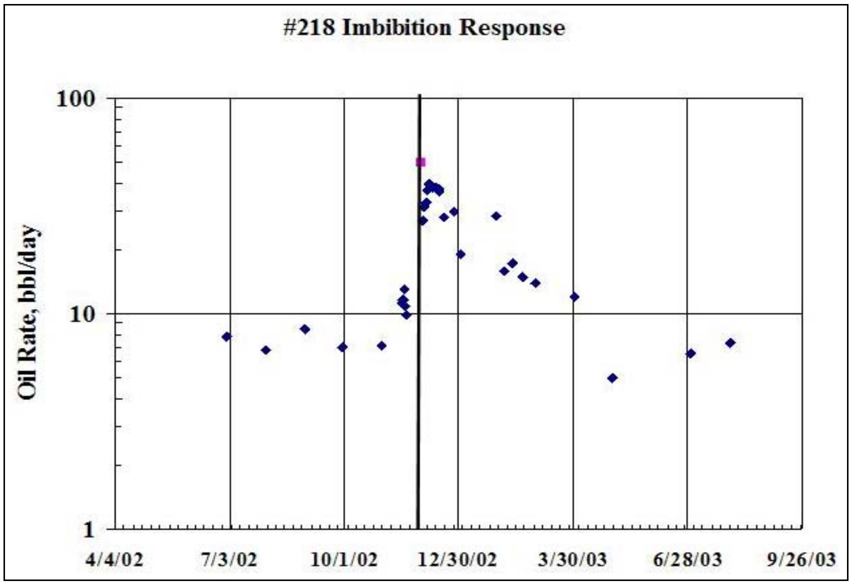


Fig. 4-4-1. Experimental well 218, oil rate vs. time.

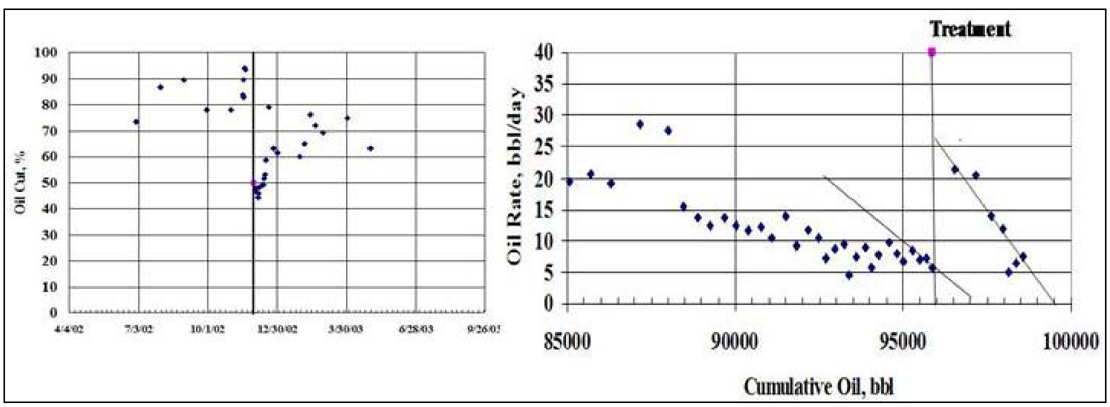


Fig. 4-4-2. Experimental well 218 oilcut vs. time and rate vs. cumulative.

The economic analysis of the field experiments did not justify expansion of the project. However, if the correlations developed during the course of this study should prove to be useful in identifying successful treatment candidates and resulted in reducing the failure rate to 20%, the incremental recovery would have been 1253 BO/well. Assuming revenue of $30/bbl after lease expense, the return would have been $37,600 on an $8,300 treatment cost. A 4:1 return is attractive. Both the fuzzy curves from the laboratory and field recovery vs. surfactant quantity support the conclusion that increased surfactant quantity increases the incremental oil. This observation could improve the economics of the technology, especially since the maximum quantity of surfactant is relatively low. The history of producing well polymer treatments supports this notion.

Section 4-5. Cationic Surfactant Field Trial

The results of a field test of the cationic surfactant, C-50, became available late in the project. Yates Petroleum Corporation field tested the C-50 surfactant soak with an application of 63 lb/ft of perforated pay in Dagger Draw well State Com. #5. The laboratory oil recovery results of the nonionic surfactant were superior to the cationic, but mixing the high pour point, nonionic surfactant in the field was difficult. The cationic surfactant caused no handling problems.

The Dagger Draw field is located in the extreme northwestern part of the Permian Basin of New Mexico near Artesia. The field produces sour, light brown, 45 ^{o}API crude from dolomite intervals in a limestone reef at about 7800 ft. The reservoir temperature was 130 ^{o}F.

The 7130 bbl of 1,340 ppm cationic surfactant solution was gravity fed down the well over a 5-day period. The well was shut-in for an 11-day soak period. The results are shown in Fig. 4-5-1.

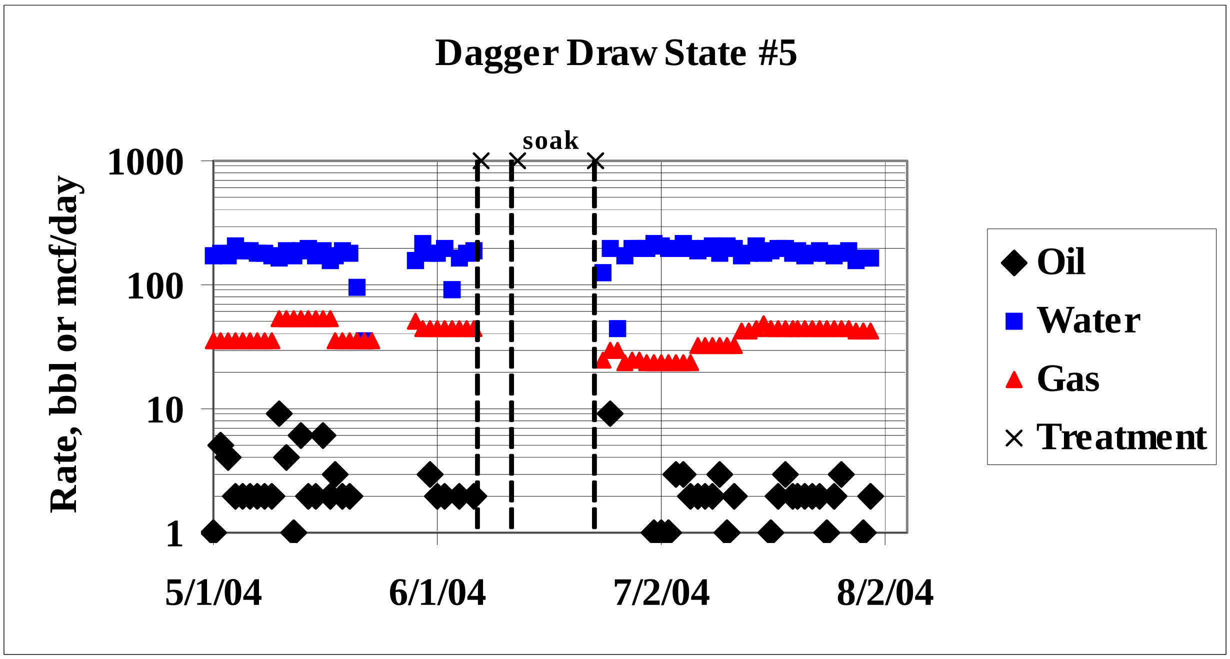


Figure 4-5-1. Cationic surfactant field test.

Field test results support the laboratory observation that the cationic surfactant improves water imbibition chiefly by lowering the IFT. Only 1 day of incremental oil was produced, suggesting that once the surfactant is produced, the wettability of the rock reverts to its original state.

State #5 has a 220-ft section of dolomite. The standard deviation of the gamma ray log is 21.1 and 0.04 for the neutron porosity log through the 220-ft interval. These values plus the 63 lb/ft value for surfactant were used as input to the neural network used to generate Fig. 4-3-3. The network predicted zero incremental oil if 63 lb/ft of the nonionic surfactant was used. Increasing the quantity of nonionic surfactant to 560 lb/ft would result in 15 BOPD of incremental oil.

Chapter 5. Commercialization

Section 1. Course of Action

Foresight Science and Technology in New Bedford, MA, conducted a Commercialization Assessment (see Executive Summary) for the technology being developed in this project. They concluded that the technology could be commercialized and recommended the following: (1) contacting a number of companies who expressed interest in the technology, (2) conducting more field tests, and (3) protecting intellectual property. Their report recognizes the difficulty in getting the end user to pay for the field tests and continued laboratory evaluations.

Based on the Foresight study, the Correlations Company made overview presentations to Mull Drilling, Surtek, and Occidental Petroleum. CoreLab's interest in the technology was limited to their Business Development Manager. Interestingly, the Foresight report led to contacts with Tiorco in Denver, CO, and GelTech in Midland, TX; presentations were made to both companies. Both are small service companies specializing in applying water shutoff technology based on cross-linked polymers. Both Tiorco and GelTech are reviewing an agreement to use the technology presented in this report.

Overview presentations were also made to Range Resources and Encore Acquisitions in Ft. Worth, TX, Kinder Morgan in Midland, TX, and ConocoPhillips in Bartlesville, OK. All companies operate large numbers of San Andres wells. Range Resources and Encore Acquisitions expressed an interest in testing the surfactant soak technology in their San Andres wells.

A patent attorney has reviewed the results of the project to date and recommended a patent search, which has been done. The search company's (Patent Insights, Inc.) reply was positive, and a first draft of a patent application is complete. It is expected that a patent application will be filed during July 2004.

The executive summary prepared by Foresight Science and Technology follows. They conclude that the technology can be commercialized.

Section 2. Foresight Executive Summary

Technology

1. *Description: This project will develop an innovative well stimulation technique, based on laboratory measurements of imbibition and wettability alteration coupled with artificial intelligence, to design well treatments. This technology works on a single well basis. The methodology first determines which surfactants will work best for a given oil or gas field, and then with the use of fuzzy ranking, determines which wells on the reservoir will have the greatest benefit from application of the surfactant. Phase I laboratory results demonstrated that the new technology works in the laboratory and that critical laboratory variables can be determined from field data. In Phase II, the laboratory experiments will be scaled-up to field experiments. Experimental wells will be selected based on bulk volume oil and porosity logs as well as other measured production parameters.*

2. *Key Innovation: The pairing of laboratory techniques and artificial intelligence for well stimulation.*

Competitive Opening

1. *Application Examined: Oil well stimulation for carbonate reservoirs.*
2. *End-User: Petroleum engineers.*
3. *Needs: End-users need simple techniques with high returns on investment.*
4. *Buying Pattern: End-user buying patterns are determined by the commodity prices of oil and gas, which are high, volatile, and unpredictable.*
5. *Drivers: Roughly half of the usable oil in the United States remains in the ground because it is not cost-effective to extract it. The cost-effectiveness of advanced stimulation and recovery techniques is, again, determined by the commodity prices of oil and gas.*
6. *Number of Competitors: There are about 3-4 advanced testing labs offering similar services (i.e., taking samples, and determining the best production techniques for a given site).*
7. *Basis for Competition: Best value.*
8. *Market Size: The number of buyers is about 8 thousand domestic small oil producers,[1] which accounts for most of the 518,805 oil wellheads in the US.[2] About 60% of the oil in the US resides in carbonate oil fields. This rate presumably holds for the individual wells, which would mean that there are about 311,283 domestic wells that could be amenable to this technology. If that rate holds for gas wells, that would be an additional 214,506 wells that this could be applied to. The number of oil wells is slowly declining, and the number of gas wells is increasing, although both numbers are fairly stable.[3]*
9. *Price:*
   a. *The use of this technology to apply surfactant should cost less than the CO_2 process. The raw CO_2 is usually \$1 per thousand ft. Some places in Texas and New Mexico can get it for as low as \$0.75-0.80 per thousand ft. An application to a field would typically require on the order of a million ft.[4] Single well application costs (including the gas and infrastructure costs) run about \$5/mcf. Service costs have to be added to this already high figure.*
   b. *Similar software for characterizing oil reservoirs runs a range of \$1600 to as much as \$40k.[5]*
10. *Other Potential Applications Identified: Other applications are areas where non-obvious patterns must be discerned from large sets of data. These kinds of capabilities are useful or required for use in bioinformatics and proteomics, customer resource management, financial data analysis, and information awareness for government. These applications would likely require a great deal of reengineering and research into end-user needs.*

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[1] Telephone conversation with A. Scott Anderson, Executive Vice President, 512-477-4452, June 25, 2003.
[2] Telephone conversation with Bob King, Energy Information Agency, 202-586-4787, June 19, 2003.
[3] *Ibid.*
[4] Telephone conversation with James R. Daniels, Vice Chairman of Producer Advisory Group, Petroleum Technology Transfer Council, General Manager at Murfin Drilling Company, 316-267-3241, June 18, 2003.
[5] Telephone conversation with Andy Benson, Engineer, StimLab, 580-252-4309, June 19, 2003.

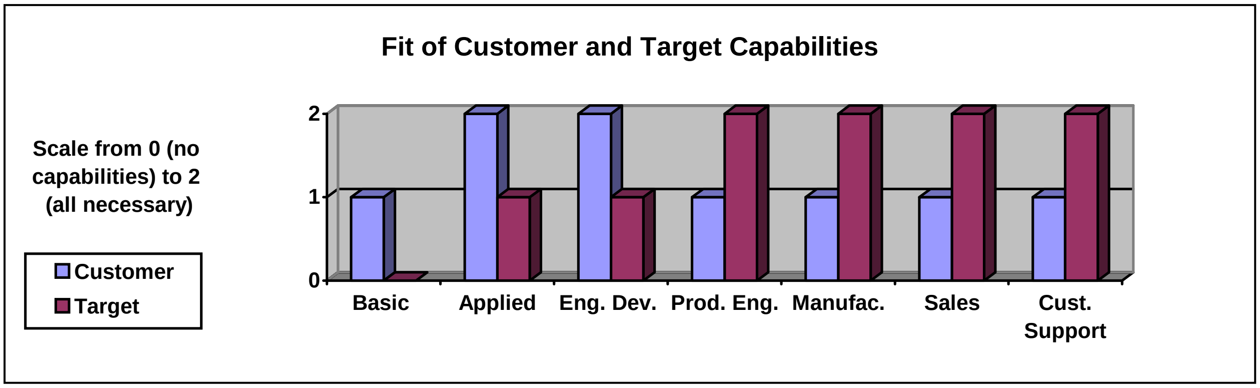
Competitive Advantage in Examined Application

1. *Competing Technologies: Competing technologies include reservoir-wide recovery enhancement with CO_2 and steam injection, and surfactant treatments at the reservoir and well levels.*
2. *Examples of Key Competitors Today: Baker Hughes, Enhanced Petroleum Resources, Schlumberger, Core Laboratories, and BJ Services.*

Price/Performance Competitiveness of Technology: We compare your technology to the offerings from Schlumberger and StimLab (a Core Laboratories company). We rate your technology at zero on all parameters simply because it has yet to be proven, and will have to be demonstrated to end-users in order for the technology to be commercialized successfully. Our particular concern is applicability, because if limited to enhancing surfactant efficacy in carbonate reservoirs, this technology would have a very limited market and value to the end-user.

Targets for Examined Application

1. *Viable Targets:*
   a. *Core Laboratories (CoreLab), Surtek, and Mull Drilling.*
   b. *We consider Occidental Petroleum (Oxy) and Schlumberger Oilfield Services and Information Solutions to be strong feasible targets. Oxy has assigned a conformance engineer to evaluate the technology. Our contact at Schlumberger is looking for the appropriate person to take Correlations' information to.*
2. *Reason for Interest in Technology: Mull Drilling is interested in looking at new technologies that can boost production. Surtek and CoreLab are interested in improving the depth of their software and consulting services.*
3. *Fit with Market: There is a ready market for improving well stimulation design.*
4. *Fit with Technology: A number of companies use a great deal of software and laboratory services for their oil and gas consulting.*
5. *Fit with Goals and Capabilities of Customer: These companies would advance the commercialization of this technology. If CoreLab remains interested they could conceivably take this technology all the way into the marketplace as a software offering or consulting service.*
6. *Likely Deal Vehicle: Mull Drilling is strictly interested in testing and demonstration of the technology. Surtek and CoreLab were not ready to discuss a likely deal vehicle.*
7. *Criteria to be Used: Return on investment, efficacy, and how applicable it is to different formations.*
8. *What Targets can Provide: All targets can provide market access and access to testing sites. Mull Drilling has about 160 wells in carbonate reservoirs that could potentially be accessible. Surtek and CoreLab are likely to provide technical assistance and may give access to client's wells and potentially well data.*
9. *General Allocation of Tasking: The chart below indicates the fit between the capabilities of the customer and the targets we found.* ***Given this fit, we feel that successful commercialization is possible.***



Entry Strategy Considerations for Examined Application

1. *General Approach: Testing and evaluation with producers is key, however, many end-users will be resistant to paying for the testing, so Correlations should pursue funding opportunities with the DOE and state organizations at the same time that it connects with the targets in this report and other producers. Also note that if Correlations were to have Surtek and CoreLab as partners it could mitigate the need for Correlations to find testing and evaluation opportunities on its own.*
2. *Fit with Market: The acceptance of this technology by end-users and others in the industry points to its good fit with the market.*
3. *Examples of Key Stakeholders: Independent Petroleum Association of America (IPAA), Petroleum Technology Transfer Council (PTTC), Texas Independent Producers and Royalty Owners Association (TIPRO), Texas Alliance of Energy Producers, Permian Basin Petroleum Association (PBPA)*
4. *Technology Action Items:*
    a. *Gather data from more test wells to establish performance and cost data in conjunction with targets and/or other stakeholders.*
    b. *Apply for a provisional patent to protect all the intellectual property behind this technology.*
5. *Marketing Action Items:*
    a. *Start contacting the stakeholders and networking organizations mentioned above and ask for their help in bringing the technology to market.*
    b. *Seek opportunities to make presentations.*
6. *Financial Action Items:*
    a. *Pursue targets.*
    b. *Seek funding from the DOE to support testing and evaluation with producers.*
7. *Market Share Goal: Assuming a partnership with one of the listed targets, Correlations can expect perhaps 1% market share at introduction (after the testing and evaluation is over), and perhaps 15-20% after five years. Deals with Surtek or CoreLab would greatly improve the chances of reaching these goals.*

Chapter 6. Discussion and Conclusions

Laboratory testing demonstrates that altering the wettability of reservoir cores from oil-wet or weakly water-wet to more water-wet results in spontaneous imbibition of water and resulting countercurrent displacement of oil. The cores in this project were saturated with reservoir fluids, and the tests were performed at reservoir temperature. Three reservoir systems and one outcrop system with reservoir fluids were examined using imbibition cells to measure oil recovery with reservoir brine followed by dilute solution of surfactants. Cationic and nonionic surfactants were tested in the reservoir systems. One reservoir and the outcrop systems proved to be water-wet; thus, no incremental oil was recovered. Nevertheless, the results demonstrated the benefit of laboratory work prior to field testing. Conventional crossplots of experimental parameters versus oil recovery were difficult to interpret; however, fuzzy curves suggested a definite relationship between cationic surfactant quantity (concentration) and incremental oil recovery.

The outcrop core experiments with reservoir fluids were intended as a means to screen a variety of candidate surfactants. Unfortunately, the laboratory procedure did not result in an oil-wet system. Thus, the performance of a dozen additional surfactants is unknown. The laboratory evidence and the surfactant cost justified testing the nonionic surfactant in the Phosphoria formation of the Cottonwood Creek field located in the Bighorn Basin of Wyoming.

A total of 24 wells with and without acid wellbore cleanups were subjected to nonionic surfactant soak treatments. The treatment results were mixed. Fuzzy curves of the surfactant volume and quantity versus the incremental oil suggested that quantity was an important variable. In fact, treatments of less than 20 lb per foot of pay are not effective. Development of a robust neural network to predict treatment results was hampered by the limited number of test wells. Nevertheless, a 3-2-1 neural network trained and tested adequately, and was used to design treatments to maximize incremental oil recovery. The network using gamma ray and neutron log statistical attributes indicated that the quantity of surfactant required to generate a 15 BOPD increase varied from 5–110 lb/ft of pay.

The economics of the field experiments did not support expansion of the program at Cottonwood Creek. However, if the neural network correlations developed during this study reduced the failure rate of future surfactant soak treatments to 20%, a 4:1 return on treatment costs would be expected.

A Commercialization Assessment Report developed by Foresight Science and Technology in New Bedford, MA, states that the technology is viable by their standards. As recommended by Foresight, interested service companies have been contacted, additional field tests are planned for the San Andres formation in the Permian Basin, and a patent application will soon be filed.

Publications

Two publications resulted from the work supported by this SBIR grant:

1. Weiss, W.W., Xie, X., Weiss, J.W., Subramaniam, V., Taylor, A. and Edens, F. Artificial intelligence used to evaluate 23 single-well surfactant soak treatments. SPE/DOE 89457 presented at the SPE/DOE 14th Symposium on Improved Oil Recovery, Tulsa, OK, April 17–21, 2004.
2. Xie, X., Weiss, W.W., Tong, Z. and Morrow, N. Improved oil recovery from carbonate reservoirs by chemical stimulations. SPE/DOE 89424 presented at the 14th Symposium on Improved Oil Recovery, Tulsa, OK, April 17–21, 2004.

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References

Ali, M., Chawathé, A., Ouenes, A. Cather, M. and Weiss, W.W. Extracting maximum petrophysical and geological information from a limited reservoir database. Paper presented at the Fourth International Reservoir Characterization Technical Conference, Houston, TX, March 2–4, 1997.

Balch, R.S., Stubbs, B.S., Weiss, W.W. and Wo, S. Using artificial intelligence to correlate multiple seismic attributes to reservoir properties. SPE 56733 presented at the SPE Annual Technical Conference, Houston, TX, October 3–6, 1999.

Chen, H.L., Lucas, L.R., Nogaret, L.A.D., Yang, H.D. and Kenyon, D.E. Laboratory monitoring of surfactant imbibition using computerized tomography. SPE 59006 presented at the International Petroleum Conference and Exhibition, Villahermosa, Mexico, Feb. 1–3, 2000.

Craig, M.D. Oil recovery process employing cyclic wettability alteration. US patent 4842065, 1988.

Du, Y., Weiss, W.W., Xu, J., Balch, R.S. and Li, D. Obtain an optimum artificial neural network model for reservoir studies. Paper 84445 presented at the SPE Annual Conference, Denver, CO, October 5–8, 2003.

Graham, J.W., McCardell, W.M., Osoba, J.S. and Richardson, J.G. Method of increasing oil production. US patent 2792894, 1953.

Hirasaki, G. and Zhang, D.L. Surface chemistry of oil recovery from fractured, oil-wet, carbonate formation. SPE 80989 presented at the SPE International Symposium on Oilfield Chemistry, Houston, TX, February 5–8, 2003.

Ma, S., Morrow, N.R. and Zhang, X. Generalized scaling of spontaneous imbibition data for strongly water-wet systems. J. Pet. Sci. Eng. 18, 165–178, 1997.

Standnes, D.C. and Austad, T. Wettability alteration in low-permeability chalk. Mechanism for wettability alteration from oil-wet to water-wet using surfactants. Presented at the 6th International Symposium on Reservoir Wettability and its Effect on Oil Recovery, Socorro, NM, September 27–28, 2000.

Stone H.L., Graham, J.W. and Blackwell, R.J. Oil recovery from fractured matrix reservoirs. US patent 3498378, 1970.

Subramaniam, V. Evaluation of well completion opportunities in the Lower Brushy Canyon using neural networks. MS Thesis, New Mexico Tech, Socorro, NM, 2002.

Weiss, W.W., Wo, S. and Balch, R.S. Integrating core porosity and SW measurements with log values. SPE 55642 presented at the SPE Rocky Mountain Regional Meeting, Gillette, WY, May 15–18, 1999.

Xie, X. and Morrow, N.R. Oil Recovery by spontaneous imbibition from weakly water-wet rocks. Petrophysics 2 (4), 313–322, 2001.